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COMPOSITIONS FOR THE MODIFIED CLAUS REACTION**

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**EXPERIMENTAL MEASUREMENT OF EQUILIBRIUM COMPOSITIONS
FOR THE MODIFIED CLAUS REACTION**

by

YINGZHAO XU



**A thesis submitted to the faculty of Graduate Studies and Research in partial
fulfilment of the requirements for the degree of MASTER OF SCIENCE**

DEPARTMENT OF CHEMICAL ENGINEERING

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UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **EXPERIMENTAL MEASUREMENT OF EQUILIBRIUM COMPOSITIONS FOR THE MODIFIED CLAUS REACTION** Submitted by **YINGZHAO XU** in partial fulfilment of the requirements for the degree of **MASTER OF SCIENCE**.

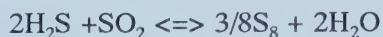
ABSTRACT

To calculate equilibrium compositions from experimental measurements at various states for the modified Claus reaction,



the composition of sulphur vapour, which is very difficult to measure, must be known in advance. Based on suggestions by Truong and others, sulphur vapour is assumed to be composed of the S_2 , S_6 , S_7 and S_8 species alone in significant amounts. The S_2 form is the most stable at high temperatures and S_8 at low temperatures. A study based solely on experimental equilibrium conversions obtained for a feed gas of specified composition (H_2S , SO_2 and N_2) at various temperatures from 286 to 359°C was carried out. By using these equilibrium conversion data and a sulphur mass balance, an experimental equilibrium constant could be calculated by assuming only a single molecular species existed in sulphur vapour. The experimental results suggest that the use of S_8 provides better agreement than from use of S_7 , S_6 or S_2 as the single species. The thermodynamically predicted and experimental conversions (the latter based upon S_8) were compared.

The resulting equilibrium constant, K_p , for the simple reaction



in the temperature range from 560 to 620 K is given by

$$\ln K_p = 13,750/T - 14.835$$

The possibility of extending this analysis to two component sulphur vapour is also discussed.

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NOMENCLATURE

A	Slope for van't Hoff equation,	K
B	Intercept for van't Hoff equation	
d_p	Catalyst particle diameter	mm
d_t	Tubing I.D.	mm
FPN_2	N_2 Flow rate in product	mol/min
FFN_2	N_2 Flow rate in feed	mol/min
FP_i	i Flow rate in product	mol/min
K_p	Equilibrium constant	
K_{p1}	Equilibrium constant for reaction $2H_2S + SO_2 \rightleftharpoons 3/8S_8 + 2H_2O$	
K_{p2}	Equilibrium constant for reaction $S_8 \rightleftharpoons 8/7S_7$	
K_{p3}	Equilibrium constant for reaction $S_8 \rightleftharpoons 4/3S_6$	
K_{p4}	Equilibrium constant for reaction $S_8 \rightleftharpoons 4S_2$	
M_i	Moles of component i	
M_{Sn}	Moles of sulphur species n	
M_T	Total moles of product	
M_{TS}	Total moles of sulphur vapour	
N_{Sg}	Total number of gram-atoms of sulphur in vapour	

N_{S_n}	Total number of gram-atoms of S_n in vapour	
P	Pressure	kPa
P_T	Total pressure	kPa
P_C	Critical pressure,	kPa
$P_{C,p}$	Pseudo critical pressure for gas mixture	kPa
P_r	Reduced pressure,	dimensionless
$P_{r,i}$	Reduced pressure for component i	dimensionless
$P_{r,p}$	Pseudo reduced pressure for gas mixture	dimensionless
R	Gas constant	kJ/(mol·K)
S.V.	Space Velocity = $\frac{\text{Vol.Feed/time@STP}}{\text{Vol.Catalyst}}$	h^{-1}
T	Temperature,	K
T_C	Critical temperature,	K
$T_{C,p}$	Pseudocritical temperature for gas mixture	K
$T_{r,i}$	Reduced temperature for component i,	dimensionless
$T_{r,p}$	Pseudoreduced temperature for gas mixture,	dimensionless
$\underline{V}$	Molar volume,	m^3/mol
$\underline{V}_C$	Critical molar volume,	m^3/mol
X	Average atomic number of sulphur vapour	
Y_i	Mole ratio of component i	
Z	Compressibility factor	
Z_C	Critical compressibility factor	
$Z_{C,p}$	Pseudocritical compressibility factor	

α	Fraction of S_8 in sulphur vapour
γ	Fractional H_2S conversion

CHAPTER I

INTRODUCTION

Acid gases containing hydrogen sulphide are often byproducts from sour gas processing or from the hydroprocessing of sulphur-containing natural fuels such as sour crude oil, residual oils, bitumen, coal and heavy oils.

Generally, the modified Claus process has been used to convert the H_2S in such acid gases to sulphur by processing in two stages: a complete or partial front-end combustion in which H_2S is oxidized involving sequential oxidation of H_2S to sulphur and then to SO_2 . The extent of oxidation is dependent upon the amount of O_2 introduced,



followed by catalytic reduction of the SO_2 in one or more stages,



Generally, the reactions (1-1) to (1-3) attain chemical equilibrium at the furnace and catalytic reactor outlets.

Even though the modified Claus reaction, (1-3), has long been of interest, to date the distribution of molecular species in sulphur vapour, which affects the determination of equilibrium constants and/or the prediction of sulphur plant performance, remains unknown. The main purpose of this work was to measure experimental conversions for the modified Claus reaction, (1-3), and to apply the results in the calculation of a suitable equilibrium constant, K_p .

1.1 RATIONALE

The use of published thermodynamic properties for all components in reaction (1-3), including the molecular sulphur species, S_2 , ..., S_8 , should enable the theoretical equilibrium conversion to be predicted. However, we do not know which combination of sulphur vapour species should be used in design calculations at converter temperatures since sulphur vapour is a mixture of unknown amounts of different homologous species. The determination of experimental conversion data for equation (1-3) should help to resolve this problem and enable one to predict the performance of sulphur plants more reliably.

1.2 PREVIOUS WORK

A review of earlier work concerning sulphur vapour is given in Chapter II. Some previous studies on experimental conversions are examined as well. Some investigators used published thermodynamic properties to predict the conversion for the modified Claus reaction. Their predicted conversions, however, tend to be somewhat lower than the experimental conversions. It was noted that even when the thermodynamic properties used are from different sources (especially for sulphur vapour), the calculated equilibrium conversions do not significantly differ. For this reason, new reliable experimental equilibrium conversion data would be useful to establish whether the predicted values may be used in engineering calculations.

1.3 OBJECTIVES

Indirectly, the purpose of the investigation is to clarify, if possible, which molecular form of sulphur vapour should be used to predict equilibrium conversions for the $\text{H}_2\text{S}/\text{SO}_2$ reaction. In this work, only reaction (1-3) will be considered to occur, i.e. the equilibrium mixture is assumed to be composed of H_2S , SO_2 , H_2O , S_n ($n=2$ to 8) and nitrogen. This assumption is reasonable since in the temperature range tested (560-620 K), other possible side-reactions, such as the cracking of H_2S to H_2 and sulphur may occur but negligibly so under the experimental conditions used herein.

This work will focus upon three main aspects: first, to study the influence of reaction variables such as temperature and feed composition upon the equilibrium conversion; second, to calculate an equilibrium constant, K_p , from the experimental conversion data (assuming a single molecular species in the sulphur vapour); and third, to discuss the possibility of extending the analysis to include a two molecular species sulphur vapour model in interpreting experimental equilibrium conversion measurements. To date, it has not been possible to measure directly by experimental means the composition of sulphur vapour.

CHAPTER II

LITERATURE REVIEW

2.1 DEVELOPMENT OF THE MODIFIED CLAUS PROCESS

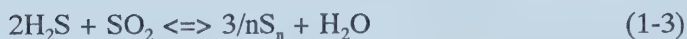
The original Claus process, developed by Carl Friedrich Claus in 1883, provided an effective way of removing hydrogen sulphide from acid gas streams. The Claus process involved the oxidation of H_2S using air in a single-step catalyst-bed at relatively low temperatures. Since the oxidation of hydrogen sulphide to sulphur is highly exothermic, the original process was limited to very small feed rates (or very large catalyst beds).

The modern two-step modified Claus process was first developed by I.G. Farbenindustrie in Germany and patented in 1932. In the modified Claus process,

(1) one-third of the H_2S gas is oxidized with air to SO_2 according to the reactions:



(2) the remaining two third of the H_2S is then allowed to react with SO_2 in the 2 to 1 stoichiometric ratio over a catalyst to produce elemental sulphur, according to



where $\text{n}=2,\dots,8$

In typical modified Claus plants, the reaction (1-3) is carried out in two or three sequential stages of catalytic converters at temperatures between 180-380°C. Typical recovery efficiencies are 90-96% for a two-stage plant and 95-98% for a three-stage plant (Cho, 1975). A typical process scheme with three catalytic reactor stages is shown in Figure 2-1. The modified Claus process has been widely utilized in industries such as

sour natural gas processing, refining of sour crude oils, processing of bitumen and heavy oils, and metal smelting.

Increasingly severe environmental legislation has regulated the minimum sulphur-containing emissions allowed to the atmosphere. To improve further the performance of modified Claus plants, some additional related processes have been developed.

The Dutch companies, Comprimó and VEG-Gasinstituut, in co-operation with the University of Utrecht, have developed one such new version of Claus process called the Superclaus process (Lagas and Berben, 1988). This Superclaus process increases the sulphur recovery rate of a Claus plant to better than 99%. Two versions have been developed: the Superclaus-99 and the Superclaus-99.5 processes.

Superclaus-99 (Lagas and Berben, 1988)(Figure 2-2) consists of a thermal stage followed by three or four catalytic reactor stages. The first two or three reactors are loaded with standard Claus catalyst but the last contains a new selective oxidation catalyst. Since the new catalyst can be operated with excess air, the final selective oxidation stage will take care of feed gas fluctuations thereby providing the flexibility needed for overall process control.

SUPERCLAUS-99.5 (Lagas and Berben, 1988) (Figure 2-3) adds a hydrogenation stage between the last Claus reactor and the selective oxidation reactor. Since all sulphur

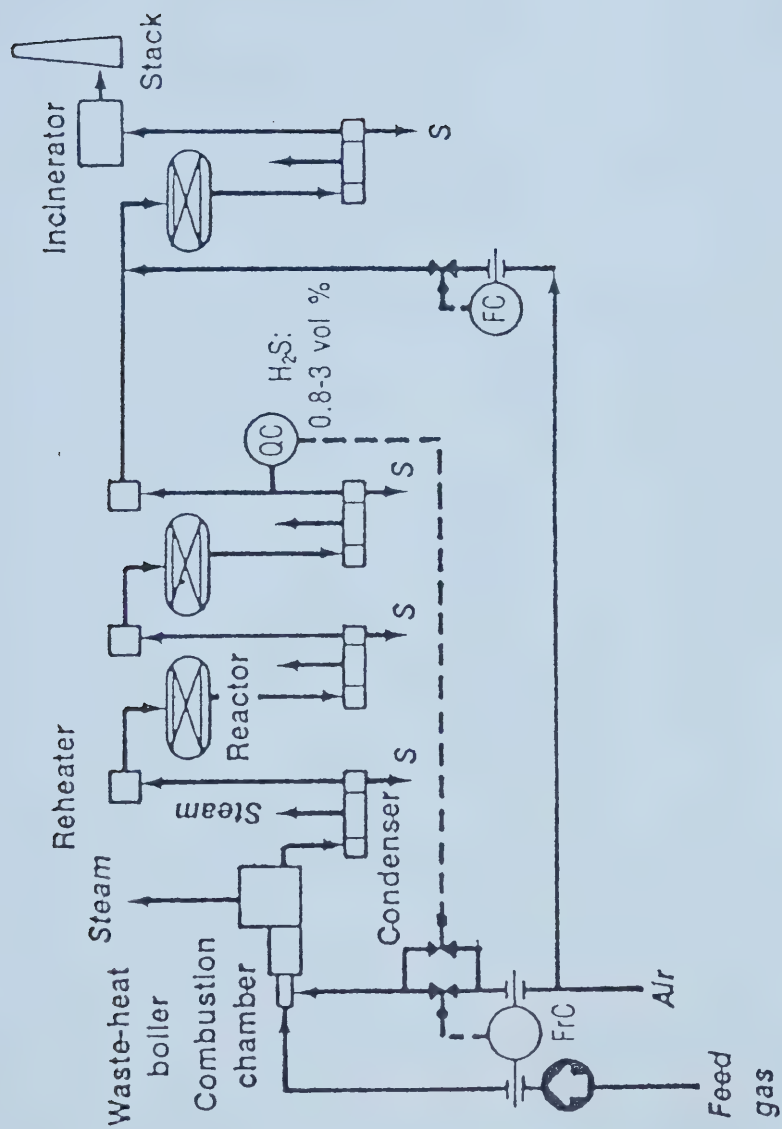


Figure 2-2 SuperClaus-99 Process (Lagas and Berben, 1988)

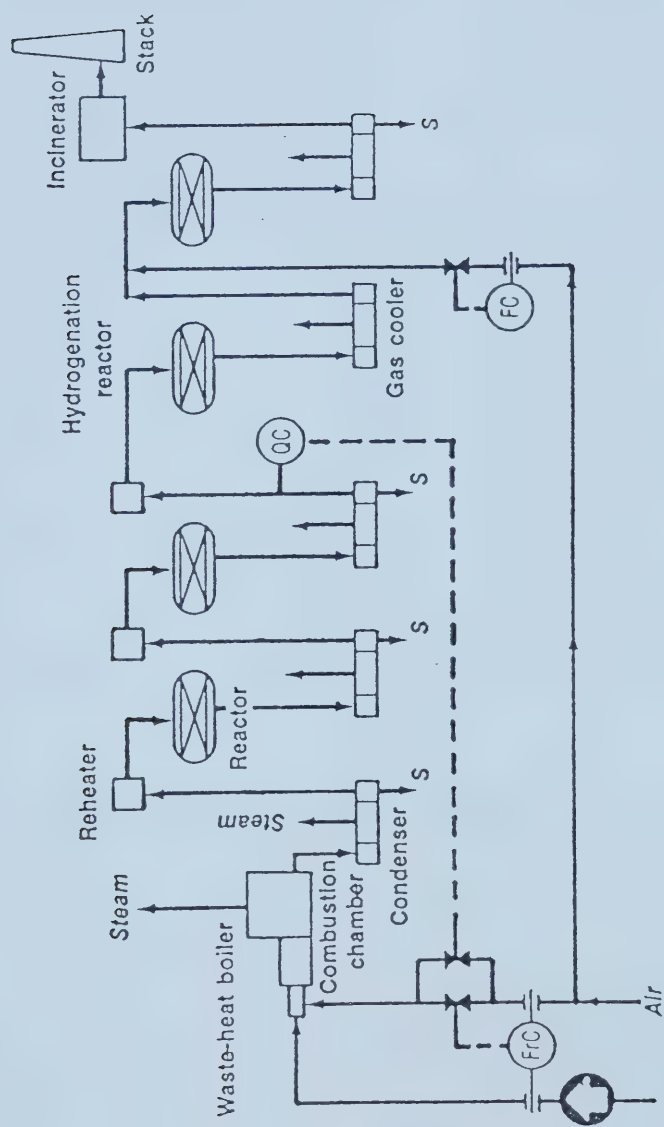


Figure 2-3 Super-Claus-99.5 Process (Lagas and Berben, 1988)

components such as SO_2 , S_n , COS , etc. are reduced to H_2S in the hydrogenation reactor (using a cobalt /molybdenum catalyst), there is no need to operate the thermal stage and the Claus reactor with excess H_2S . The normal 2:1 ratio of $\text{H}_2\text{S}:\text{SO}_2$ is usually applied but it is less critical than for normal Claus operations. The gas from the hydrogenation reactor is cooled to the optimum inlet temperature of the selective oxidation catalyst. The desired flexibility is again obtained by introducing excess air to the final Superclaus selective oxidation reactor and, as it is not sensitive to water, there is no need to condense the water vapour downstream.

The new selective-oxidation catalyst consists of active metal oxides supported on an inert carrier. It exhibits "claimed" unique properties:

- (1) H_2S is completely converted with a high selectivity into sulphur, with very small formation of SO_2 even in the presence of an overstoichiometric amount of oxygen.
- (2) The catalyst does not catalyze the Claus equilibrium reaction (1-3). This means that the catalyst is ineffective for the reverse reaction of sulphur with water to form H_2S and SO_2 .
- (3) A high water concentration in the process gas has slight influence on the conversion of H_2S into sulphur.
- (4) The catalyst is selective for H_2S oxidation. Other components such as CO , H_2 and other combustibles are not oxidized.

2.2 PRIOR STUDIES ON THE EQUILIBRIUM CONVERSION IN THE MODIFIED CLAUS REACTION AND ON THE MOLECULAR DISTRIBUTION WITHIN SULPHUR VAPOUR

Two main factors affect the calculated thermodynamic equilibrium conversion: first, the number of chemical species thought to be present at equilibrium must be specified; and second, reliable thermodynamic properties for all specified equilibrium species must be available. Studies involving thermodynamic equilibrium conversions which have been done since 1950 have been based on values of thermodynamic properties compiled from different sources. Compared to the uncertainties associated with the properties of sulphur vapour, the thermodynamic properties of other species in the Claus reaction system, like H_2S , SO_2 and H_2O , are well-established. The thermodynamic properties for all molecular species comprising sulphur vapour were not available within a single source until the JANAF, 3rd edition (1985) was published.

Since 1960, more studies of sulphur vapour have appeared probably because of scientific interest in the behaviour of molecular sulphur vapour and the need for better properties to enable one to predict the composition of equilibrium vapour over a large temperature range. In the following section, a more detailed review will be done upon studies related to sulphur vapour.

2.2.1 Sulphur Vapour

The vapour pressure of sulphur from room temperature to 2300 K was first measured by

Berkowitz (1965) and Meyer (1965). The critical temperatures reported by Baker (1971) and Rau et al. (5, 291, 1973) were within 1 K, i.e. 0.1%; however, the critical pressure cited by Baker was 200 atm, i.e. 20% larger than that reported by Rau et al. Specific heat and other thermal data for the vapour had been summarized for JANAF 2nd edition by Jensen (1973) and others.

Preuner and Schupp (1909) concluded that equilibrium vapour consists of S_8 , S_6 and S_2 . Braune and Steinbacher (1952) studied the vapour pressure and the ultraviolet spectrum of sulphur vapour and concluded that a uv absorption based at 510 nm was due to S_4 . They also observed the spectral band later attributed to S_3 . The 100-year controversy about sulphur vapour composition was finally settled when Berkowitz and Marquart (1963) showed that the vapour contains all molecules of S_n , $2 < n < 10$, including the odd-numbered species. Buchler (1966) even detected S_{12} in the vapour. The fact that photoionization yields only one ionization value (Berkowitz and Chupka, 1969) supports earlier thermodynamic reasoning (Berkowitz and Marquart, 1963) that all vapour species occur as rings.

Berkowitz and Chupka (1969) had shown by mass spectrometry that vapour in equilibrium with rhombohedral cyclohexa-S contains S_6 . Detry et al. (1967) used Rickert's electrolytic cell: $Pt, Ag | AgI | Ag_2S | Pt$, to overcome problems in identifying the molecular ionization pattern in a mass spectrometer. Thus, it became possible to unravel the molecular composition of equilibrium vapour over a large temperature range. At low

temperature, S_8 accounts for over 90% of the vapour, while S_6 and S_7 make up the rest. Upon heating, the concentration of S_8 in equilibrium vapour steadily decreases, and the vapour consists increasingly of the smaller species. Above 1000 K, S_2 is the most abundant species. The composition in the intermediate temperature range (400-1500 K), which was estimated by Meyer (1976) from Berkowitz and Chupka (1969), Detry et al. (1967), Oommen (1970), Rossini (1970), Baker (1971) and Rau et al. (5, 291, 1973) consists of S_n , $2 \leq n \leq 8$.

The relative concentrations of small species increase at less than saturated pressures. Spectral studies (Yee et al., 1972) indicated that at 800 K and 13.333 kPa, S_2 accounts for over 80% of all vapour species. At 1000 K and 0.13333 kPa, the corresponding value was 99%. S_3 and S_4 in concentrations of about 10% were obtained at about 1.3333 kPa and 800 K (Oommen, 1970). Sulphur atoms were not present in equilibrium vapour below the critical point (Baker, 1971). They could be prepared as transient species by photolysis (Fair et al., 1971).

More recently, Kaloidas and Papayannakos (1987), in their study of the $H_2S/H_2/S_j$ system, calculated the concentration of the various sulphur molecules in the sulphur vapour by means of a numerical method described by the authors. The data of Rau et al. (5, 833, 1973) for sulphur molecular species were used. They concluded that at a total pressure of 1 atm, the diatomic sulphur molecules prevail, being more than 91% above 1000 K.

From the above review, it seems that many researchers support the view that sulphur vapour contains molecules S_2 , S_6 and S_8 in the temperature range of 450-650 K which is the normal temperature range for modified Claus process (Preuner and Schupp, 1909; Braune and Steinbacher, 1952; Berkowitz and Marquart, 1963; McGregor, 1971; Meyer, 1976; Liu, 1978; Truong, 1982). In addition, the presence of S_4 (Braune and Steinbacher, 1952), S_5 (Meyer, 1976) and S_7 (Meyer, 1976) was also stated to occur in sulphur vapour in this temperature range. Since lower temperatures favour the formation of heavier sulphur molecule, we should also take S_7 into consideration. In the work to be described herein, molecules S_2 , S_6 , S_7 and S_8 will be assumed to be present in sulphur vapour in the above-mentioned temperature range.

2.2.2 The Calculation of Thermodynamic Equilibrium Conversion

Gamson and Elkins (1953) made the first detailed study of the reaction equilibria between hydrogen sulphide and air. The O_2/H_2S ratio in the starting mixture was taken to be 0.5, i.e. stoichiometric according to the reaction



which dominates the equilibrium composition. The compounds S_2 , S_6 , S_8 , H_2O , H_2S , SO_2 and N_2 , were assumed to be present in the equilibrium mixture and the authors developed a special iterative technique for solving the mass balance equation. The data of Kelley (1937) were used to establish the equilibrium constants between the various sulphur polymers, independent of the other compounds present in the mixture.

Munro and Masdin (1967) calculated equilibrium constants for reactions in the Claus system with the assumption that S_2 , S_6 and S_8 existed over the temperature range, 398-508 K, using the thermodynamic properties from JANAF (1965) and the sulphur vapour pressure of West and Menzies (1929). Their experimental conversions are less than or equal to their calculated conversions for feeds with less than 20% by volume of water vapour. They mentioned that the thermodynamic equilibrium conversion is sensitive to values of the free energy used in the calculations.

Ericksson and Rosen (1968) regarded the data of Kelley (1937) as inaccurate. They employed White's free energy minimization technique and, in addition to the compounds considered by Gamson and Elkins (1953), they also assumed S_4 , H_2 , O_2 , H_2S , SO_2 and SO_3 to be present at equilibrium over the temperature range 550-650 K. They used the JANAF thermodynamic properties (1965) and the equilibrium constants for S_4 , S_6 , S_8 formed from S_2 of Braune and Steinbacher (1952).

Bennett and Meisen (1973) calculated the equilibrium constants of H_2S /Air system using the thermodynamic data taken from JANAF 2nd Ed. (1971), the measurements for sulphur species of Detry et al. (1967), and the free energy for H_2S_2 of Mackle and O'Hare (1963). They assumed 40 species were contained in the equilibrium mixture over the temperature range, 600-2000 K. However, they found that only 25 species were predicted to be present in greater than 0.1 ppm. Their result is intermediate to the predictions made by Gamson and Elkins (1953) and McGregor (1971).

McGregor (1971) and Liu (1978) used a free energy minimization method to predict equilibrium compositions. They assumed that only S_2 , S_6 and S_8 were present in sulphur vapour over the temperature range, 400-1600 K, for the H_2S /air reaction in stoichiometric ratio and used the thermodynamic properties listed by McBride (1963) and Kelley (1937). They also included the possible formation of H_2 but ignored the presence of other oxidation products. Their calculated equilibrium conversions are slightly higher than those predicted by Gamson and Elkins (1953).

Truong (1982), using properties from JANAF 2nd Ed. (1971) and Rau et al. (5, 833, 1973), also calculated thermodynamic equilibrium conversions by means of the free energy minimization method. For simplicity, the author assumed only H_2S , SO_2 , H_2O , N_2 , S_2 , S_6 and S_8 to be present at equilibrium. Experimental conversion data of Cho (1975), the most recent, were compared to her calculated thermodynamic equilibrium conversions. The same conclusion was advanced that the experimental conversions are higher than the calculated thermodynamic values. To study the influence of error from the thermodynamic data used to calculate thermodynamic equilibrium conversions, Truong (1982) conducted a series of sensitivity studies for each species in terms of their standard heats of formation and standard entropies. From comparing the effect of a 10% deviation from standard heat of formation reference value for each of S_8 , S_2 , H_2S , SO_2 and H_2O , the error in predicted conversion was least for H_2O , followed by SO_2 , S_2 , H_2S and S_8 in that order. While considering the effect of error in standard entropy, H_2S was the most sensitive, and then H_2O , S_2 , S_8 and SO_2 . Truong also pointed out in her survey of

thermodynamic properties, that the properties of water vapour, H_2S and SO_2 were likely determined most accurately because of their availability from different reactions.

2.2.3 The Measurement of Experimental Conversion

In their investigation of conversions in the Claus reaction, Gamson and Elkins (1953) used a catalytic reactor which comprised a 38.1 mm I.D. sillimanite tube, 94.4 cm long, heated electrically by means of Nichrome resistance wire. The catalyst bed occupied the middle 45.7 cm. The catalyst used was -4+8 mesh Porocel, an activated bauxite with low iron content and 2% volatile content. The stoichiometric $\text{H}_2\text{S}/\text{SO}_2$ mixture was reacted at three temperatures, 230, 260 and 300°C, over space velocities ranging from 240 to 1920 h^{-1} . The results of Gamson and Elkins are tabulated in Table 2-1.

Cho (1975) adopted a similar but smaller integral fixed-bed reactor which was fabricated using a 316 stainless steel tube of 25.4 mm I.D. and 22.9 cm long. A γ -Alumina (Kaiser-201) was used as catalyst. The conversions are shown in Table 2-2. The work of Gamson and Elkins and that of Cho differed in the magnitude of space velocities used. Cho used values as low as 4 h^{-1} , ranging upwards to 100 h^{-1} ; whereas, Gamson and Elkins used a higher flow rate corresponding to a space velocity of 250 h^{-1} . Figure 2-4 shows the conversion vs temperature curves for the data of both Gamson and Elkins (1953) and Cho (1975).

The reactor designs of both Gamson and Elkins and Cho and the exothermicity of the

reaction (3-1) suggest that difficulties in measuring the temperature of the catalyst bed might affect the accuracy or reliability of the calculated conversion results. First, their reactor diameters were 38.1 and 25.4 mm, respectively. This may not be small enough to insure a uniform radial temperature distribution (Dalla Lana, Personal Communication, 1993) and could lead to a discrepancy between measured temperature and actual reaction temperature. Since the reaction is exothermic, the bed interior could be higher in temperature than the reactor tube wall temperature. Under such conditions, the use of the wall temperature as the bed temperature leads to too high a corresponding measured conversion. On the other hand, the conversion data of Gamson and Elkins (1953) at a space velocity of 240 h^{-1} should have been lower than or equal to the values of Cho (1975) at 100 h^{-1} . The opposite result was observed which creates some doubt about the reliability of both sets of data.

According to Li (1986), when the ratio of d_t to d_p is greater than 5, the radial temperature gradient may be safely neglected. Since the ratio of d_t to d_p in this work was about 4.1 ($d_p=1.2 \text{ mm}$, $d_t=4.93 \text{ mm}$), it might not be large enough to neglect radial temperature profile. However, since the reactor tubing extended 304.8 cm (10 feet), irrespective of radial temperature profile formed in the catalyst bed while the reaction (1-3) was proceeding, thermal and chemical equilibrium were attained at the oven temperature at tubing outlet (Chapter V documents tests to ensure that chemical equilibrium was established at the reactor outlet).

TABLE 2-1RESULTS OF GAMSON AND ELKINS (1953)

Temperature (K)	Space Velocity (h^{-1})	Conversion (%)
503	240	97.9
533	240	96.7
573	240	94.8

TABLE 2-2RESULTS OF CHO (1975)

Temperature (K)	Space Velocity (h^{-1})	Conversion (%)
550	100	95
575	100	92
604	100	88
657	100	85
703	100	77
555	4	98
604	4	97
658	4	89
660	4	89
702	4	89

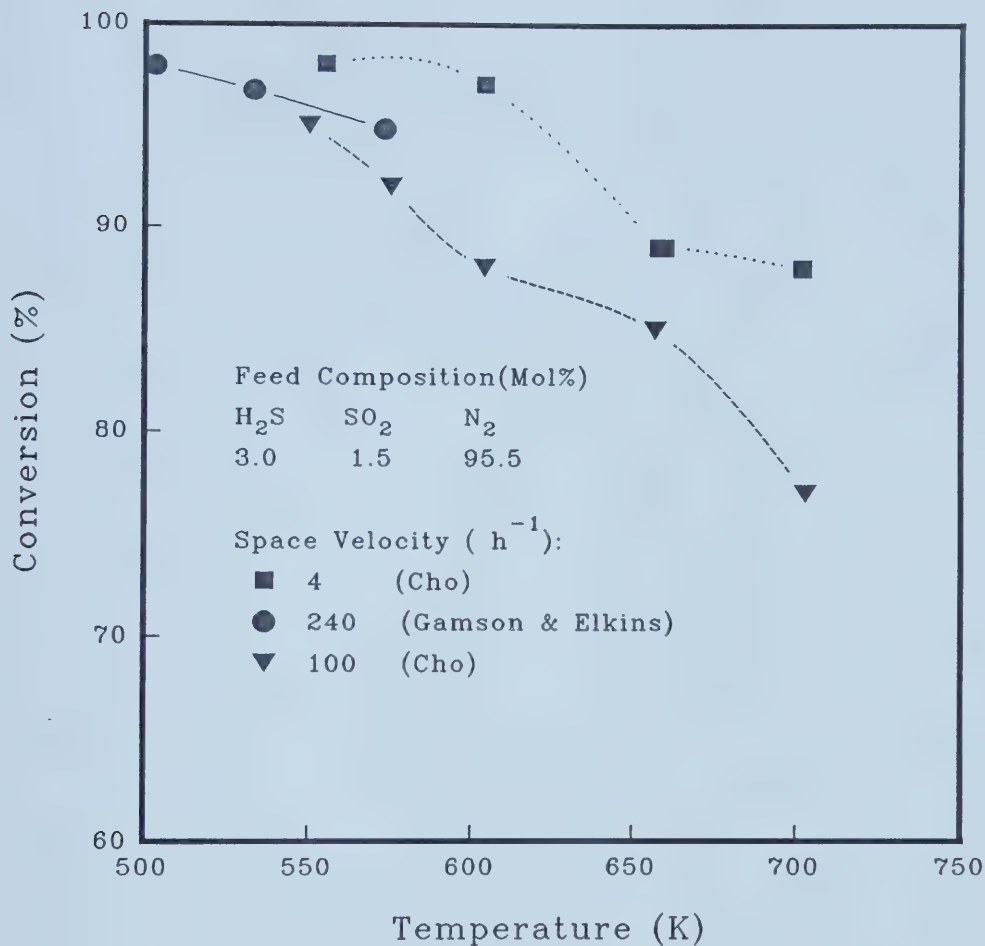


Figure 2-4 Conversion Data from Gamson & Elkins (1953) and from Cho (1975)

CHAPTER III

THEORY

3.1 REDUCTION OF DATA

3.1.1 Ideal Gas Law Assumption

The ideal gas law was applied in all calculations in this study and the validity of its use will now be discussed.

3.1.1.1 The Law of Corresponding States and the Compressibility Factor

The reduced properties for a pure component system can be expressed by the following:

$$P_r = P/P_c \quad (3-1)$$

$$T_r = T/T_c \quad (3-2)$$

$$\underline{V}_r = \underline{V}/\underline{V}_c \quad (3-3)$$

where the subscripts, r and c symbolize the reduced and critical properties, respectively.

We now introduce the compressibility factor

$$Z = \underline{PV}/RT \quad (3-4)$$

as a measure of deviation of real gas behaviour from that of an ideal gas. The compressibility may be expressed in terms of the reduced variables,

$$Z = \frac{P_r \underline{V}_r}{RT_r} \frac{P_c \underline{V}_c}{T_c} \quad (3-5)$$

The term $P_c \underline{V}_c / RT_c$ is the compressibility at the critical point, Z_c , so equation 3-5 becomes

$$Z = Z_c \frac{P_r \underline{V}_r}{T_r} \quad (3-6)$$

Since the law of corresponding states suggests that $\underline{V}_r$ should be a universal function of P_r and T_r then equation (3-6) implies that the compressibility factor should also be a universal function of P_r and T_r for all gases that have the same critical compressibility. Examination of the critical properties (P_c , $\underline{V}_c$, and T_c) of most real gases indicates that their critical compressibilities fall within a fairly restricted range, $0.25 \leq Z_c \leq 0.31$. Thus the law of corresponding states indicates that the compressibility factors for most real gases should be essentially a universal function of P_r and T_r .

In an effort to increase the accuracy of results obtained from the law of corresponding states, many attempts have been made to add a third correlating parameter in addition to P_r and T_r . The most widely accepted of these third parameters appears to be the critical compressibility, Z_c . Thus Z is often presented as a function of P_r , T_r , and Z_c rather than simply P_r and T_r . Most correlations that do not use Z_c as a parameter employ the constant, $Z_c=0.27$, which appears to be a reasonable value for Z_c when no other information is available. In the absence of better information, this latter rule will be employed in this work.

3.1.1.2 Mixtures of Reactant and Product Gases

Although the P - $\underline{V}$ - T properties of many real pure gases are tabulated in the literature, e.g. handbooks such as that by Perry and Chilton (1973), the added degree of freedom for mixtures of gases (due to variations in composition) makes it unrealistic to attempt to tabulate P - $\underline{V}$ - T properties for gas mixtures.

Consequently, if the P-V-T properties of a gas mixture are required, it is usually necessary either to make experimental measurements or, more simply, to use one of the available rules for predicting these properties based upon information on the pure components.

In this study, we employed an empirical rule, the "pseudocritical law", that provides a convenient means for estimating the compressibility factor of a gaseous mixture. This rule states that "pseudocritical" properties for a mixture are calculated from the critical properties of the components present in the mixture as follows:

$$P_{c,p} = \sum y_i P_{c,i} \quad (3-7)$$

$$T_{c,p} = \sum y_i T_{c,i} \quad (3-8)$$

$$Z_{c,p} = \sum y_i Z_{c,i} \quad (3-9)$$

where the subscript p indicates a pseudocritical property (the critical properties of pure components concerned are presented in Table 3-1). These pseudocritical properties may then be used to compute a pseudoreduced temperature and pressure for the mixture:

$$T_{r,p} = T/T_{c,p} \quad (3-10)$$

$$P_{r,p} = P/P_{c,p} \quad (3-11)$$

The assertion is then made that the mixture behaves as if it were a single species at these reduced conditions. The compressibility factor for the mixture is determined from the generalized compressibility charts in the usual fashion. Now, we use this approach to predict the behaviour of reactant and product mixtures which were involved in this work.

Reactant Mixture

There were three different feed compositions employed in the experimental work. Their values along with the ranges of reaction temperature and pressure are shown in Table 3-2. The calculation of pseudocritical and reduced properties for each group are given in Table 3-3.

Product Mixture

Because of the similarity in composition of the product mixtures, one product mixture is used as an example. For a feed condition of H_2S : 5.0%, SO_2 : 2.5% and N_2 : 92.5%, reaction pressure of about 101.33 kPa and lowest reaction temperature, 558.6 K, the corresponding H_2S equilibrium conversion of 93.18% assumed and an average sulphur atomic number about 7.0 (please refer to Chapter V and Appendix C for the information). The product composition and their corresponding pseudo properties are shown in Tables 3-4 and 3-5.

For the pseudo reduced properties for the feed and product shown in Tables 3-3 and 3-5 and the corresponding compressibility factor values obtained from Figure 3-1 (generalized compressibility factor charts for $Z_c=0.27$), (Balzhiser et al., 1972), it is apparent, even considering the effect of the slightly higher Z_c values in our study ($Z_{c,\text{max.}}=0.288$), that the compressibility factor for all such mixtures would closely approximate 1.00, which suggests that use of the ideal gas law is acceptable under these conditions. Accordingly, throughout this work, the equation of state for ideal gases was employed. For a mixture

TABLE 3-1CRITICAL PROPERTIES OF PURE COMPONENTS

	H ₂ S	SO ₂	N ₂	H ₂ O	S
T _C (°C)	100.4	157.2	-147.1	374.0	1040
P _C (kPa)	9008.24	7873.34	3394.56	22059.54	11754.28
Z _C	0.283	0.268	0.289	0.220	0.263

TABLE 3-2REACTION CONDITIONS

Group No.	H ₂ S	SO ₂	N ₂	T(min.)	P(kPa, max.)
1	5.0%	2.5%	92.5%	558.6 K	111.46
2	7.6%	3.8%	88.6%	558.6 K	111.46
3	10.0%	5.0%	85.8%	558.6 K	111.46

TABLE 3-3FEED MIXTURE PSEUDOCRITICAL AND REDUCED PROPERTIES

Group No.	T _{c,p} (K)	P _{c,p} (kPa)	T _{r,p} (min.)	P _{r,p} (max.)	Z _{c,p}
1	146.00	3787.72	3.83	2.94x10 ⁻²	0.288
2	156.37	3991.39	3.57	2.79x10 ⁻²	0.288
3	165.97	4179.86	3.37	2.67x10 ⁻²	0.287

TABLE 3-3
PRODUCT DISTRIBUTION

Feed Composition: H_2S SO_2 N_2
 5.0% 2.5% 92.5%

Maximum Reaction Temperature: 558.6 K

Reaction Pressure: 111.46 kPa (max.)

H_2S Conversion: 93.18%

Average Sulphur Atomic number: 7.0

$Y_{\text{H}_2\text{S}}$	Y_{SO_2}	$Y_{\text{H}_2\text{O}}$	Y_{S}	Y_{N_2}
0.35%	0.18%	4.80%	1.03%	93.64%

TABLE 3-4
PRODUCT MIXTURE PSEUDOCRITICAL AND REDUCED PROPERTIES

Group No.	$T_{c,p}(\text{K})$	$P_{c,p}(\text{kPa})$	$T_{r,p}(\text{min.})$	$P_{r,p}(\text{max.})$	$Z_{c,p}$
1	164.65	4665.23	3.39	0.0233	0.284

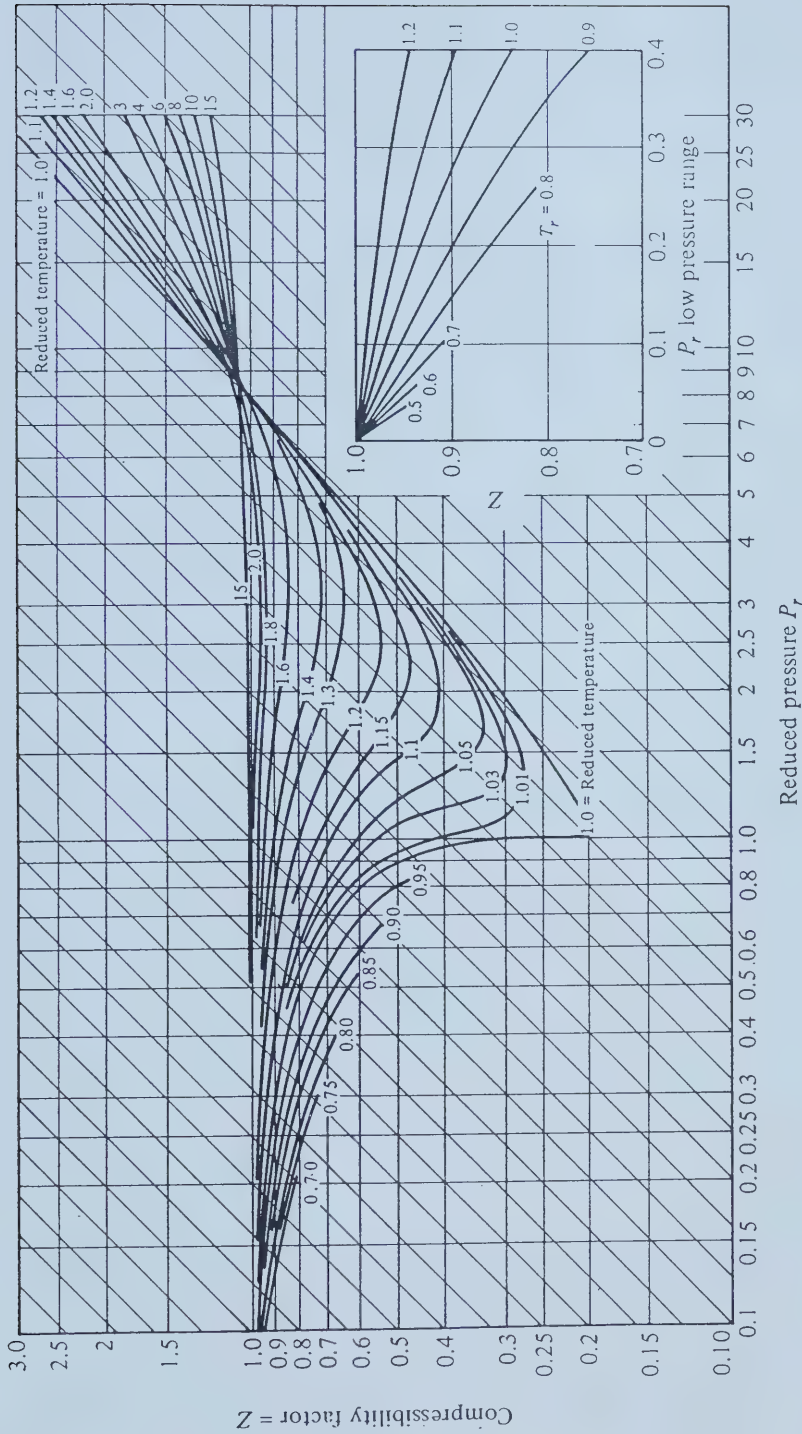


Figure 3-1 Generalized Compressibility Factor Chart for $Z_c = 0.27$ (Balzhiser et al., 1972)

of ideal gases, the mole fractions, volume fractions and partial pressures as a fraction of total pressure are all equal and this useful fact has also been employed.

3.1.2 Reactor Material Balance

It was assumed that N_2 passed through the laboratory reactor as an inert component, so the product flow rate of N_2 equals that entering the reactor, $FP_{N_2} = FF_{N_2}$. Therefore the product flow rates of H_2S , SO_2 and H_2O can be expressed as,

$$\begin{aligned} FP_i &= (FP_{N_2})(Y_i/Y_{N_2}) \\ &= (FF_{N_2})(Y_i/Y_{N_2}) \\ &= FF_{N_2}(M_i/M_{N_2}) \end{aligned} \quad (3-12)$$

where $i = H_2S, SO_2$ and H_2O

The fractional H_2S conversion (γ) can then be calculated as follows:

$$\gamma = \frac{\left[\frac{(M_{H_2S})}{(M_{N_2})} \right]_{Feed} - \left[\frac{(M_{H_2S})}{(M_{N_2})} \right]_{Product}}{\left[\frac{(M_{H_2S})}{(M_{N_2})} \right]_{Feed}} \quad (3-13)$$

For the stoichiometric H_2S/SO_2 ratio of 2:1, as per equation:



the following relationships could be obtained from (3-12):

$$FP_{H_2O} = FF_{H_2S} - FP_{H_2S} \quad (3-14)$$

$$FP_{SO_2} = 0.5(F_{H_2S} - FP_{H_2S}) \quad (3-15)$$

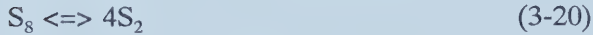
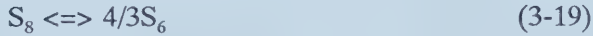
and in unit time, assuming $n=2, 6, 7$ and 8 ,

$$\begin{aligned} N_{S_g} &= 8M_{S_8} + 7M_{S_7} + 6M_{S_6} + 2M_{S_2} \\ &= 1.5(F_{H_2S} - FP_{H_2S}) \end{aligned} \quad (3-16)$$

where N_{S_g} and M_{S_n} are total number of gram-atoms of sulphur and moles of sulphur molecular species, S_n , in the product mixture, respectively.

3.2 DETERMINATION OF EXPERIMENTAL EQUILIBRIUM CONSTANTS

If, as discussed in Chapter II, the presence of S_2 , S_6 , S_7 and S_8 in sulphur vapour is assumed, then the modified Claus reaction (3-1) would involve the following reactions at equilibrium,



According to equations (3-17) to (3-20), their equilibrium constants, K_{P1} to K_{P4} , respectively, are defined as follows:

$$K_{P1} = \frac{P_{H_2O}^2 P_{S_8}^{\frac{3}{8}}}{P_{H_2S}^2 P_{SO_2}} = \frac{\left[\frac{M_{H_2O}}{M_T} \right]^2 \left[\frac{M_{S_8}}{M_T} \right]^{\frac{3}{8}}}{\left[\frac{M_{H_2S}}{M_T} \right]^2 \left[\frac{M_{SO_2}}{M_T} \right]} P_T^{-\frac{5}{8}} \quad (3-21)$$

$$K_{P2} = \frac{P_{S7}^{\frac{8}{7}}}{P_{S8}} = \frac{\left[\frac{M_{S7}}{M_T} \right]^{\frac{8}{7}}}{\left[\frac{M_{S8}}{M_T} \right]} P_T^{\frac{1}{7}} \quad (3-22)$$

$$K_{P3} = \frac{P_{S6}^{\frac{4}{3}}}{P_{S8}} = \frac{\left[\frac{M_{S6}}{M_T} \right]^{\frac{4}{3}}}{\left[\frac{M_{S8}}{M_T} \right]} P_T^{\frac{1}{3}} \quad (3-23)$$

$$K_{P4} = \frac{P_{S2}^4}{P_{S8}} = \frac{\left[\frac{M_{S2}}{M_T} \right]^4}{\left[\frac{M_{S8}}{M_T} \right]} P_T^3 \quad (3-24)$$

Since the product mixture was assumed to behave like an ideal gas mixture, then the partial pressures could be calculated using Dalton's Law:

$$P_j = y_j P = (M_j / \sum M_j) P_T \quad (3-25)$$

Where j denotes the molecular species in the product mixture and P_T stands for total reaction pressure. Unlike M_{H_2S} , M_{SO_2} and M_{H_2O} , the value of M_{S_n} ($n=2,6,7,8$) cannot be obtained directly from the mass balance; the latter only identifies the total number of sulphur gram-atoms formed. If the four values of M_{S_n} could be specified, then the total molecular number contained in the product mixture would be expressed as:

$$M_T = \sum M_j \quad (3-26)$$

And finally, the four values of K_p , (3-21) to (3-24), would then be obtained.

3.2.1 Assumption of Sulphur Molecular Model of Single Species

Since we can only obtain the total number of sulphur gram-atoms from the experimental conversion data and mass balance, an assumption of sulphur vapour comprising a single molecular species is necessary to calculate the total moles of sulphur vapour in the product mixture from equation (3-16). For example, if we adopt S_8 , equation (3-16) becomes:

$$N_{Sg} = 8M_{S8} \quad (3-27)$$

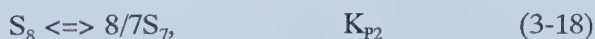
the total moles in the product mixture, M_T , will then be

$$M_T = M_{H2S} + M_{SO2} + M_{H2O} + N_{Sg}/8 \quad (3-28)$$

each term on the right side of equation (3-28) can be calculated from the H_2S conversion data and the mass balance, enabling K_p to be calculated. This approach will be used in interpreting the experimental equilibrium conversion in this study. A more detailed example calculation procedure is shown in Chapter V and Appendix C.

3.2.2 Assumption If Sulphur Vapour Comprises Two Molecular Species

Because of the limitation in experimental information, in the preceding section, K_p could be calculated only for sulphur vapour comprising one molecular species. In this section, we examine the possibility of including two molecular species in the sulphur vapour. Using S_7 and S_8 molecular species, the modified Claus reaction is described by two equilibrium equations,



As shown in the preceding section, from the experimental conversion of H_2S and the sulphur mass balance, the total number of gram-atoms of sulphur (N_{Sg}) can be calculated.

Accordingly,

$$N_{Sg} = N_{S8} + N_{S7} \quad (3-29)$$

$$N_{S8} = \alpha N_{Sg} \quad (3-30)$$

$$N_{S7} = (1-\alpha)N_{Sg} \quad (3-31)$$

where, N_{S8} = gram-atom number of S_8

N_{S7} = gram-atom number of S_7

α = fraction of N_{Sg} which is S_8

then, in equations

$$K_{P1} = \frac{\left[\frac{M_{H2O}}{M_T} \right]^2 \left[\frac{M_{S8}}{M_T} \right]^{\frac{3}{8}}}{\left[\frac{M_{H2S}}{M_T} \right]^2 \left[\frac{M_{SO2}}{M_T} \right]} P_T^{-\frac{5}{8}} \quad (3-21)$$

$$K_{P2} = \frac{\left[\frac{M_{S7}}{M_T} \right]^{\frac{8}{7}}}{\left[\frac{M_{S8}}{M_T} \right]} P_T^{\frac{1}{7}} \quad (3-22)$$

$$M_{S8} = \alpha N_{Sg}/8 \quad (3-32)$$

$$M_{S7} = (1-\alpha)N_{Sg}/7 \quad (3-33)$$

and

$$M_T = M_{H2S} + M_{SO2} + M_{H2O} + \alpha N_{Sg}/8 + (1-\alpha)N_{Sg}/7 \quad (3-34)$$

M_T : total moles in products mixture

Thus, K_p will be a function of the unknown fraction, α . If the total moles of sulphur vapour (M_{ST}) were known,

$$M_{ST} = M_{S8} + M_{S7} = \alpha N_{Sg}/8 + (1-\alpha)N_{Sg}/7 \quad (3-35)$$

the unknown, α , could be calculated and subsequently, values for K_{p1} and K_{p2} . In Chapter VI, a possible means of measuring total moles of sulphur vapour will be suggested. From the above analysis, it is evident that each additional sulphur molecular species introduced will need one more piece of independent experimental information to enable one to solve for the various M_i . In other words, to determine K_{p1} to K_{p4} , three more independent experimental measurements will be needed.

3.3 THE FREE ENERGY MINIMIZATION PROGRAM

The free energy minimization program used in this study was written originally by McGregor (1971) and modified by Tong (personal communication, 1993). The program calculates the equilibrium composition of a chemical system by minimizing the total free energy of the system from the input species mole numbers and the molar free energy of each species present in the initial and final compositions. In the free energy minimization method only the standard free energies of each species at certain temperature are needed. Those interested in the principles and the numerical methods are referred to the thesis of McGregor (1971).

CHAPTER IV

DESCRIPTION OF THE EXPERIMENTAL EQUIPMENT

The experimental equipment consisted of three major sections: the reactant feed system, the reaction system and the analysis system. These systems were originally designed and built by Yung under the direction of Dr. I. G. Dalla Lana. To make the original equipment operational, considerable modifications were required in each system. A complete schematic diagram is given in Figure 4-1.

4.1 REACTANT FEED SYSTEM

The gas feeds were supplied from gas cylinders, each equipped with its own pressure regulator. Each gas stream was dried by DAVISON M562B Molecular Sieve contained in a 500 cm³ stainless steel cylinder. An Oxy-PurgeTM N oxygen trap was attached to the N₂ line to remove O₂ which could react with H₂S at room temperature or, perhaps, poison the catalyst.

One Matheson 8200 mass flow controller was used to control the flow rate of the N₂ stream. Two Sierra, SidetrapTM mass flow controllers with special Teflon packing and seals inside were used to measure the flow rates of H₂S and SO₂. Calibrations for the three mass flow controllers are presented in the Appendix B.

The reactants were blended in a mixing venturi to form a feed mixture of desired composition. Their combined gauge pressure was measured by a Heise Solid Front-C-53329 gauge.

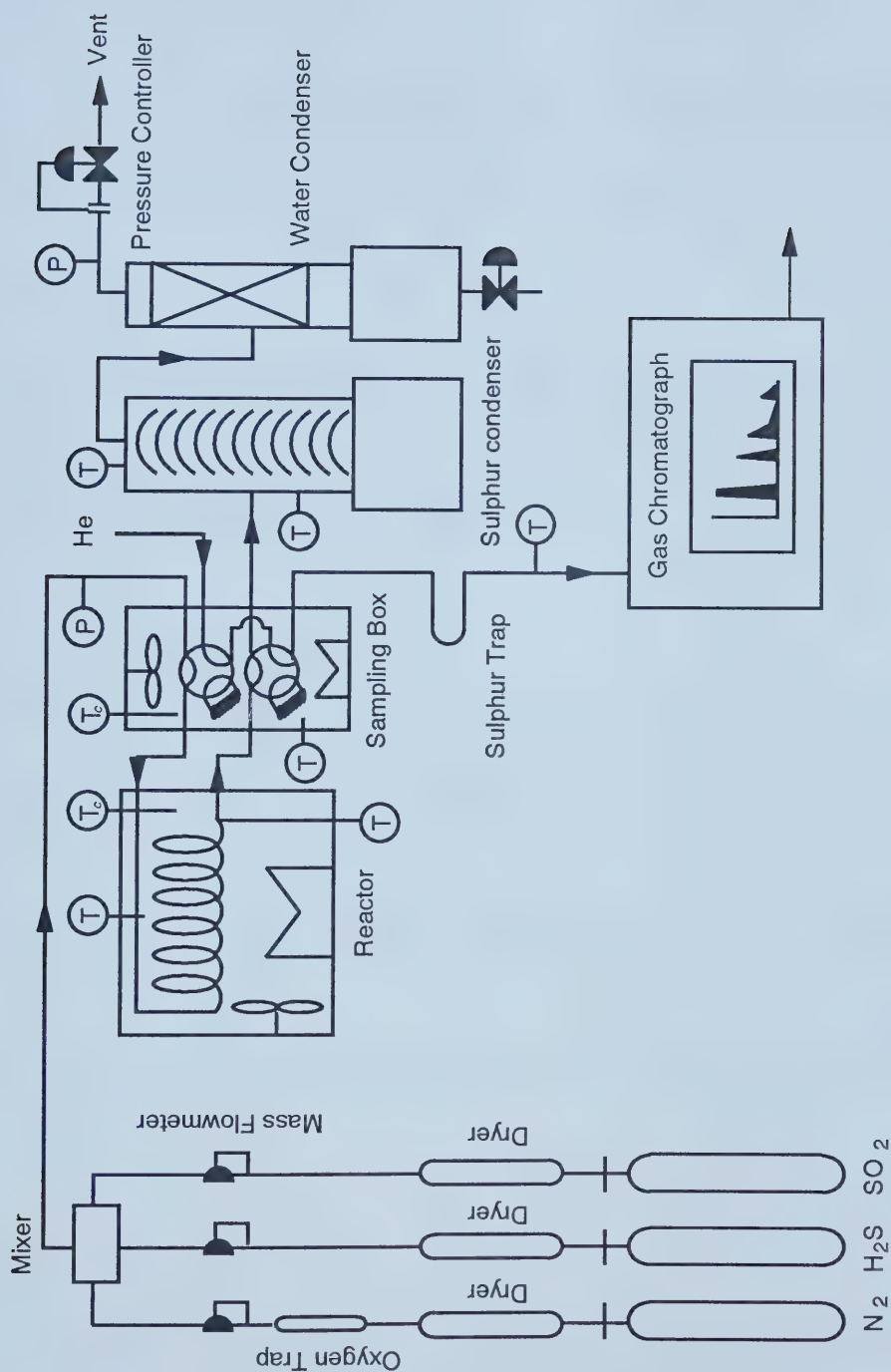


Figure 4-1 Schematic Diagram of Experimental Apparatus

4.2 MATERIALS

4.2.1 Feed Gases

The reactant gases, H_2S and SO_2 , were bought from Matheson Co., and the N_2 was purchased from Linde Co. The purities specified by the suppliers are listed in Table 4-1.

4.2.2 Catalyst

The catalyst used in this work was Kaiser-201 γ -alumina manufactured by Kaiser Aluminum and Chemical Sales Inc. The properties of the Kaiser-201 catalyst as specified by the manufacturer are presented in Table 4-2.

4.3 REACTION SYSTEM

The reaction system originally comprised two reactors, a sulphur condenser, a water condenser and a sulphur trap. The use of two reactors was first designed by Yung to enable the measurement of equilibrium conversions simultaneously at two different temperatures for the one inlet feed stream. Due to the high pressure drop observed across the two reactors in sequence and the fact that the supply pressure of SO_2 gas in the cylinder could only reach about 322 kPa, only one reactor shown in Figure 4-1 was used in this study.

4.3.1 Reactor

The reactor tube having an inside volume of about 58 cm^3 was a 6.35 mm O.D. x 304.8 cm long coil, fully packed with crushed -12+16 mesh Kaiser-201 Catalyst. The oven

TABLE 4-1

PURITIES OF GASES

N ₂	99.99% min.
H ₂ S	99.50% min.
SO ₂	99.98% min.

TABLE 4-2

STANDARD CATALYST PROPERTIES (KAISER 201)

Surface area:	380 m ² /gram
Chemical composition on dry basis:	
SiO ₂	0.020%
Fe ₂ O ₃	0.020%
TiO ₂	0.002%
Na ₂ O ₃	0.300%
Al ₂ O ₃	93.600%
Ignition loss	6.000%

housing the reactor was insulated using 310 ceramic foam insulation material, covered by a thin stainless steel plate. Two Chromalox SE 1003 strip heaters (400 W each) were used to heat the compartment. A 10.16 mm fan associated with a Magnetek CB2G011N motor was used to circulate the air inside. Two thermocouples, mounted at the reactor outlet and at the 243.84 cm position along the reactor, respectively, were used to monitor the equilibrium temperature. Within the reaction temperature range tested (560-620 K), the isothermal oven temperature could be maintained within $\pm 0.2^\circ\text{C}$ of the set temperature.

4.3.2 Sulphur Condenser, Water Condenser and Sulphur Trap

The product stream from the reactor was divided into two parts: the first portion entered the sulphur condenser and then the water condenser before being vented, while the remainder of the stream entered the sulphur trap to remove the product sulphur vapour before reaching the GC analysis system.

The sulphur condenser was made of stainless steel pipe of 50.8 mm inside diameter and 50.8 cm inch length containing internal baffles. The temperature of the condenser was maintained at about 250°C at the inlet and 110°C at the outlet so that the product sulphur vapour might be condensed, which helped to maintain a flow of the gaseous product mixture without any serious plugging by solid sulphur. The condenser wall was wound with nichrome wire to provide the heat to maintain the condenser temperature. It has been pointed out that H_2S and SO_2 might dissolve in the presence of liquid water and thus it was necessary to maintain the sulphur condenser above the water dew-point. This

stream was cooled in the water condenser to remove water separately prior to being vented.

The water condenser was made of stainless steel pipe of 50.8 mm in inside diameter and 30.48 cm length, and packed with glass wool. The condensed water was allowed to flow by gravity into the bottom of the condenser to be accumulated before being discharged through a vent valve attached to the bottom of the condenser. The product stream, stripped of the sulphur and water, then passed through the side opening to reach the reactor back pressure control valve on the vent line.

A sulphur trap was designed to remove the product sulphur vapour before the product stream entered the GC analysis system. The two sulphur traps were made of a stainless steel 316 tube of 12.7 mm O.D. and 25.4 cm in length in a U shape. No baffle was provided in the sulphur trap to reduce the dead zone around the base of the baffles which could cause the broader residence time distribution of the product stream in the trap. Each sulphur trap was alternately used while the other was undergoing cleaning of the accumulated sulphur. On the outlet of the sulphur trap, a filter made of glass wool was packed in about 1.27 cm in depth to avoid any entrainment of dusty sulphur particles upstream to the GC.

4.3.3 Process Pressure Measurement and Control

As mentioned in 4.1, the upstream (inlet) pressure of the reactor was measured at the

feed mixture venturi by means of a Heise Solid Front-C-53329 gauge. The back (outlet) pressure of the reactor could be measured after the water condenser using the same gauge and could be controlled by a FOXBORO 69PA-1 valve at vent along with a FOXBORO 611AH electronic transmitter. The outlet pressure was used to specify the reaction pressure in this study, which was about 101.33 kPa.

4.4 FEED-PRODUCT ANALYSIS SYSTEM

The compositions of both feed and product gas streams were analyzed by a Hewlett Packard 5710A gas chromatograph equipped with a Hewlett Packard 3380A integrator.

4.4.1 Separation of Components in GC Column

To separate all components in the gaseous reactant or product mixtures, the GC column was arranged in a two-column-in-series mode. All of the components, N_2 , H_2S , SO_2 and H_2O were separated using two columns in series; the first column was a 243.84 cm Porapak Q in 50-80 mesh, and the second a 121.92 cm Porapak R in 50-80 mesh (Wilhite and Hollis, 1968). Both columns were fabricated by 3.18 mm diameter SS 316 tubing. The Porapak Q (243.84 cm) column was almost capable of performing the desired separation completely. The only separation it would not do adequately was water from hydrogen sulphide. To separate the water from hydrogen sulphide, a shorter section of Porapak R (121.92 cm) was added to the Porapak Q column (243.84 cm). This combination retained the water long enough to separate it from hydrogen sulphide without seriously affecting the separation or retention times of the other components. The feature

of the separation of each peak is illustrated in Figure 4-2. Since the water peak always tended to tail, which would affect the accuracy of SO_2 analysis, H_2S had to be taken as the basis to calculate experimental conversion in this study. GC calibrations for H_2S and SO_2 are given in the Appendix B.

4.4.2 Sampling Compartment and Sampling Valve Mode

One 6-way valve and one 10-way valve were used to sample the feed and product streams. An oven, shown in Figure 4-1 was fabricated to house the sampling valves. Heated air inside this compartment was circulated by means of a three-inch diameter fan and its temperature was measured by thermocouple and controlled by an Omega CN380 temperature controller. The range of temperature measurement is room temperature to 400°C and the control accuracy is 0.1°C .

4.4.3 Sampling valve setting

Figure 4-3 shows how the two sampling valves function. At position 1, both feed and product samples are carried into coils on the 6 and 10-port valves, respectively. The feed sample is then analyzed by switching the 6-port valve to position 2 while the 10-port valve is still kept at position 1. Similarly, the switching of the 10-port valve to position 2 enables one to analyze product sample while keeping 6-port valve at position 1.

Figure 4-2 Gas Chromatograph

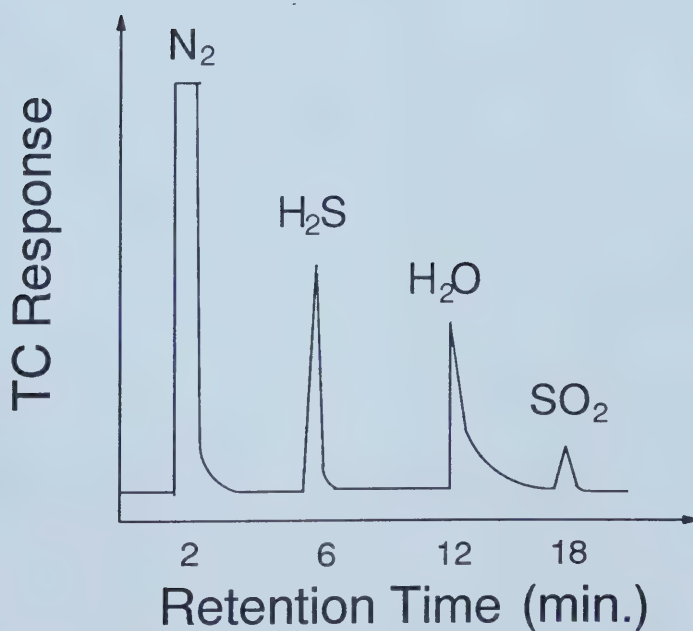
Detector: Thermal Conductivity

He Regulator Pressure: 56 psig

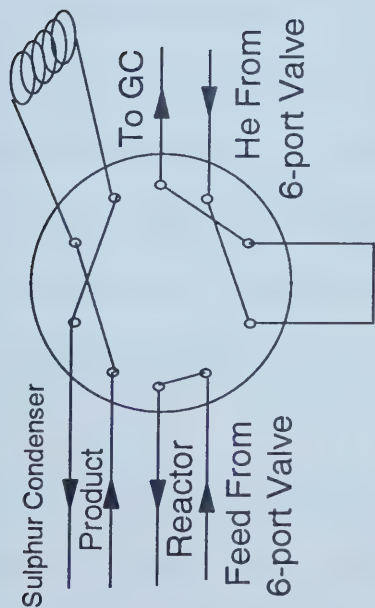
Flowrate: 56 ml/min. (He)

Oven Temperature: 75 °C

Detector Temperature: 100 °C



Position1



Position2

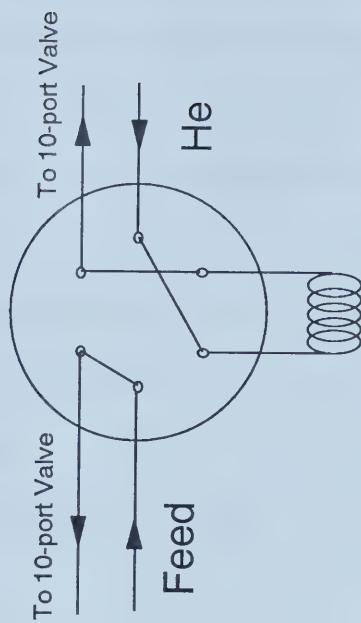
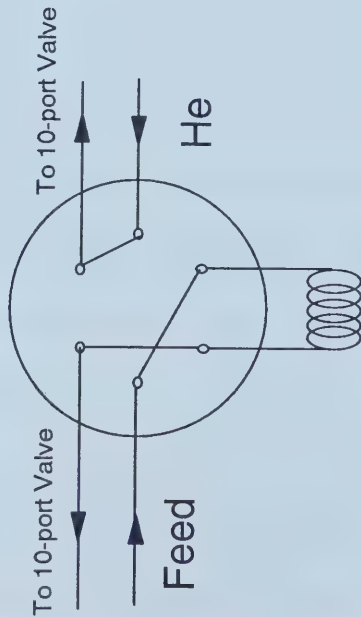
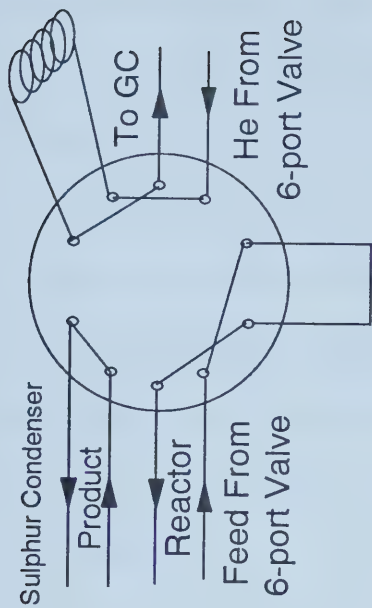
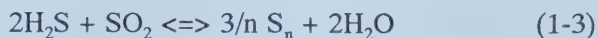


Figure 4-3 Sampling Valve Setting

4.5 OPERATION OF EQUIPMENT AND EXPERIMENTAL PROCEDURES

The experimental work dealt mainly with measuring conversions for the reaction,



using an integral fixed-bed coil type reactor packed with Kaiser-201 catalyst over a variety of conditions as follows:

- 1) For given feed composition and pressure, study influence of temperature.
- 2) For given temperature and pressure, study influence of changes in concentration level of stoichiometric mixture of H_2S - SO_2 .
- 3) For given temperature and pressure, study influence of non-stoichiometric ratio of H_2S and SO_2 .

4.5.1 Startup of the system

After all of the equipment was assembled, the threaded joints and fittings were checked for leakage by means of SNOOP liquid at a nitrogen pressure of around 377.16 kPa within the system. The outlet of the system was closed, the N_2 cylinder was isolated, and the N_2 pressure within the system was expected to remain constant for about 4 hours to ensure negligible gas leakage from the whole system.

When the system was proved gas-tight, the outlet was hooked up to the vent and the N_2 cylinder valve was then opened to start a flow of N_2 through the system. All heating elements were then switched on. With both the N_2 flow and heating started, the flow of He was initiated through carrier and reference sides in the GC system. To pretreat the

GC column, it was heated at 170°C for about 1 hour. After turning on both GC oven and the detector filament, it took about 2 hours for the GC oven to reach thermal equilibrium at 75°C, and more than 4 hours for the detector at 100°C. During the gas chromatogram base-line adjustment, the attenuation ratio was set at the maximum sensitivity, i.e. at minimum attenuation ratio, on both the gas chromatograph and the integrator. The base-line adjustment could be checked numerically on the integrator printout.

4.5.2 Catalyst Treatment and Experimental Runs

At the beginning of an experimental run, a flow of N₂ whose flow rate was equal to that of the total reaction feed flow was introduced. In the meantime, temperatures for the sampling and reactor ovens were set at 200°C and the desired reaction temperature, respectively. Once both temperatures were approaching steady-state, usually after about three hours, the reactor inlet pressure was measured and the outlet value was set by the pressure controller such that the mean value of the inlet and outlet pressures equalled the desired reaction pressure (later, when the feed mixture was introduced, only a fine adjustment of the outlet pressure was required to maintain the desired reaction pressure).

When the above steps were successfully accomplished, the flow of H₂S gas was introduced at the desired rate. The pressure regulator for the H₂S cylinder was set at about 322 kPa. Next, the SO₂ gas cylinder was turned on with its pressure regulator set at about 322 kPa. The flow rates of N₂, H₂S and SO₂ then were adjusted using the mass flow meters to obtain the desired total flow rate and feed composition.

After the reactor outlet temperature stabilized, the feed and product streams were individually analyzed repeatedly by the gas chromatograph until three consecutive reproducible results for each stream were obtained. When the feed and the product compositions remained constant, it was assumed that the reaction system had reached a steady-state. The conversion, based on the difference between H_2S contents of the feed and product streams, was regarded as an experimental equilibrium conversion (the validation of this will be discussed in the Chapter V). From the previous work (Liu, 1978), the required time after which the reaction system was believed to have reached equilibrium was about 1.5 hours. To be conservative, the reaction was allowed to proceed for more than 3 hours before the analysis was started.

In making consecutive runs requiring two successive days, in which either the temperature of the reactor or the feed composition was changed, N_2 purging through the whole system was maintained overnight. Then, the reaction procedures were reset on the following day as per the procedures mentioned above.

The experimental data thus obtained included the reactor inlet and outlet pressures, the reactor outlet temperature, the feed flow rates and the area ratios for separated peaks in the gas chromatogram.

4.5.3 Shutdown Procedures

When a complete set of runs was finished and/or repair work had to be done because of

equipment failure, the reactant flows with the exception of N_2 were stopped. The N_2 was kept flowing through the system overnight to completely purge any remaining reactants and products. After complete purging, all power supplied to the system was switched off to cool the system to room temperature.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

5.1 EXPERIMENTS TO TEST IF EQUILIBRIUM CONVERSION ATTAINED

Since the measurement of experimental equilibrium conversion was crucial to this study, a series of test runs was made to select a suitable space velocity to ensure attainment of chemical equilibrium. The feed mixture consisted of 7.6 mole % H_2S , 3.8 mole % of SO_2 and the balance, N_2 . A typical experimental run required about 3 hours. The reactions were carried out at temperatures of 559 and 610 K, and at three different space velocities, 242, 364 and 486 h^{-1} based upon inlet flow at standard temperature and pressure.

From the results presented in Figure 5-1, it can be seen that in the region of space velocity from 242 to 486 h^{-1} , the conversion was essentially constant at constant temperature. The average space velocity of 364 h^{-1} and a reaction time of three hours were selected as the conditions to be used throughout this experimental work to ensure attainment of experimental equilibrium conversion (the raw and processed data are shown in the Appendix D).

5.2 EXPERIMENTAL DATA

5.2.1 Conversion versus Temperature

The influence of temperature (286-358°C) was studied at constant feed composition and pressure. Later, three different inlet compositions were introduced. The results, as plotted in Figure 5-2, 5-3 and 5-4, show that at outlet pressure and given feed composition, the conversion decreased with increase in temperature over the range tested, which agrees with the trend to be expected for a reversible exothermic reaction.

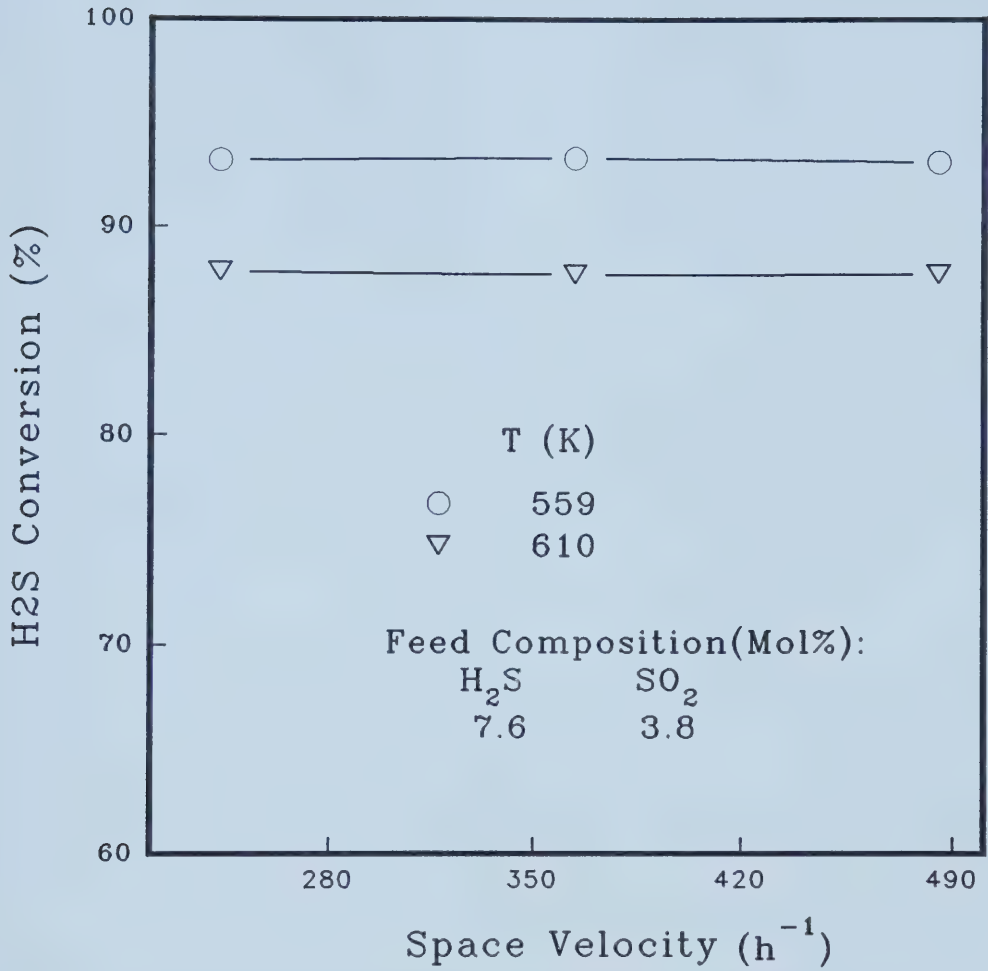


Figure 5-1 Experimental Verification
of Equilibrium

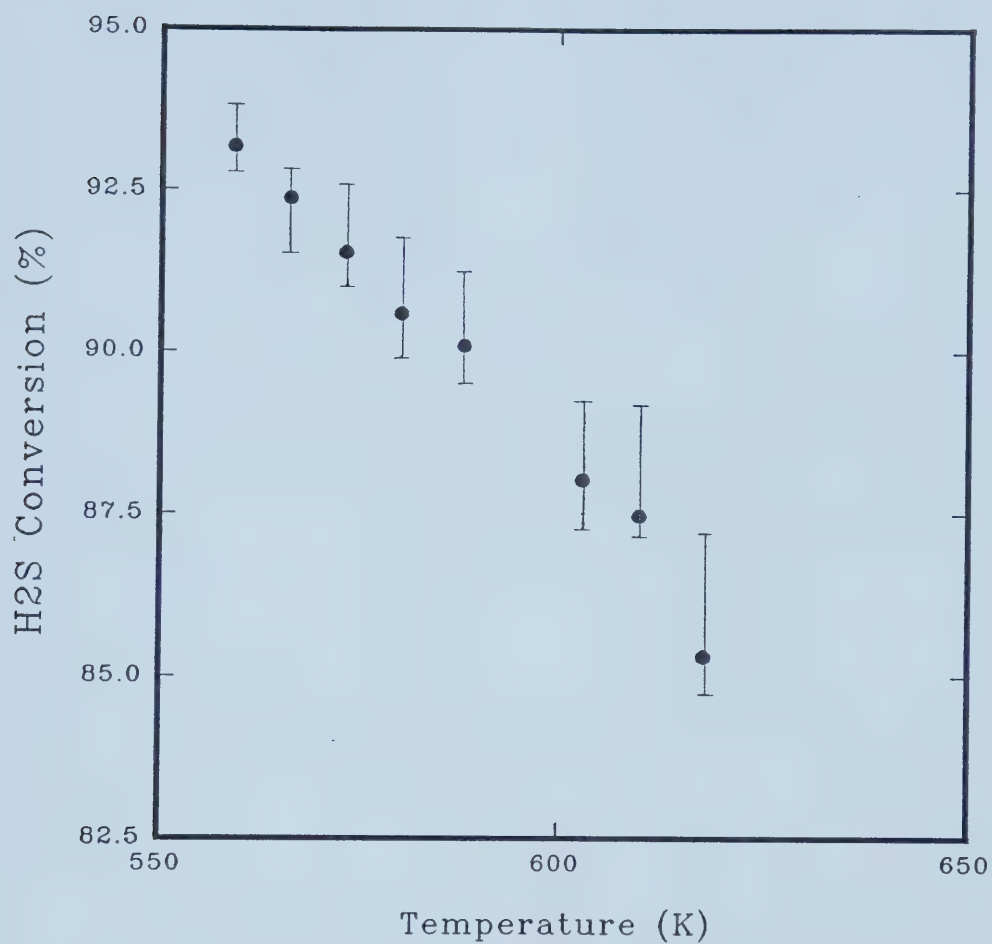


Figure 5-2 Conversion vs Temperature

for Feed Composition of H₂S: 5.0%,

SO₂: 2.5% and N₂: 92.5%

Space Velocity(h⁻¹): 364

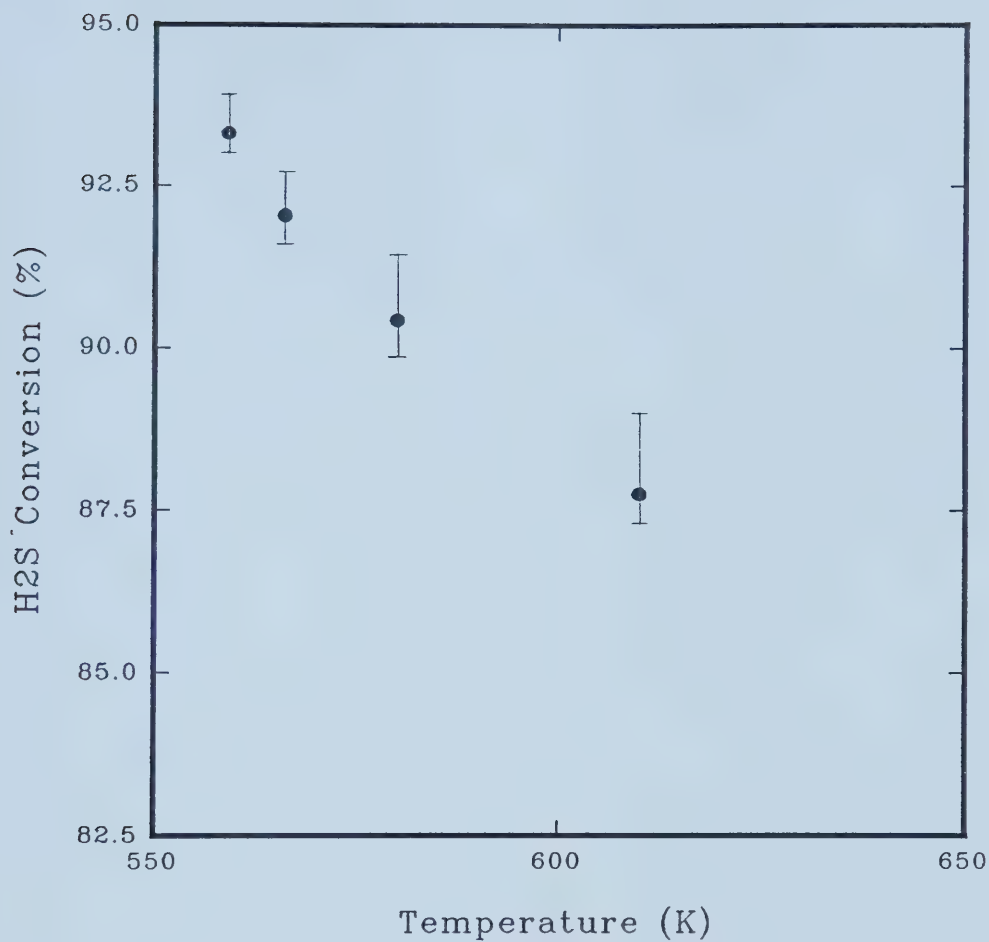


Figure 5-3 Conversion vs Temperature

for Feed Composition of H₂S: 7.6%,

SO₂: 3.8% and N₂: 88.6%

Space Velocity(h⁻¹): 364

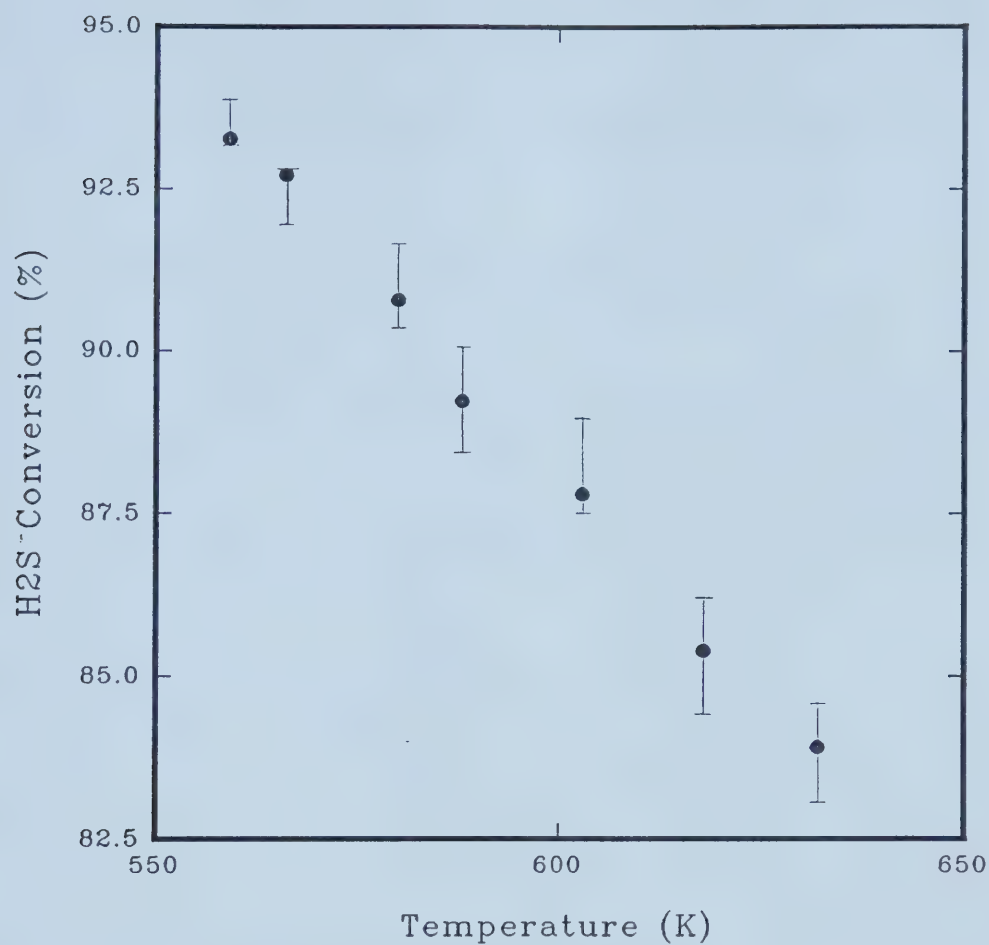


Figure 5-4 Conversion vs Temperature

for Feed Composition of H₂S: 10.0%,

SO₂: 5.0% and N₂: 85.0%

Space Velocity(h⁻¹): 364

Error bounds were introduced in Figures (5-2) to (5-4) by considering the errors involved in (a) calibrations of mass flow controllers; (b) accuracy of these controllers themselves; and (c) calibration of GC (please see Appendix F for detailed error analysis).

5.2.2 Conversion versus Stoichiometric Feed Composition

The influence of stoichiometric feed composition upon conversion was studied in a series of experimental runs at different temperatures. Figure 5-5 indicates that the conversion remained almost constant with increasing feed concentration, and the limited experimental data presented also suggest that the two plots (different composition) intersect. When the trend of Figure 5-5 is considered in terms of experimental error (see Figures 5-2 and 5-4), however, the intersection cannot be considered to be significant. In fact, parallel lines may be drawn within error bounds shown. The position of these lines can be manipulated, still within the error bounds, to position the two lines above or below each other. Accordingly, one cannot distinguish the differences in the trends for the different H_2S feed composition because of the error involved.

At temperatures below 800 K, the thermodynamic equilibrium conversion shown in Figure 5-6 predicts a slight increase in conversion when a higher inlet $\text{H}_2\text{S}/\text{SO}_2$ concentration is introduced. Figure 5-6 shows the relationship between conversion vs temperature at different inlet concentrations based upon an assumed presence of S_2 , S_6 , S_7 and S_8 molecular species in sulphur vapour. If we divide the temperature range from the Figure 5-6 into two parts: $T < 800 \text{ K}$ and $T > 800 \text{ K}$, two different conversion trends can be

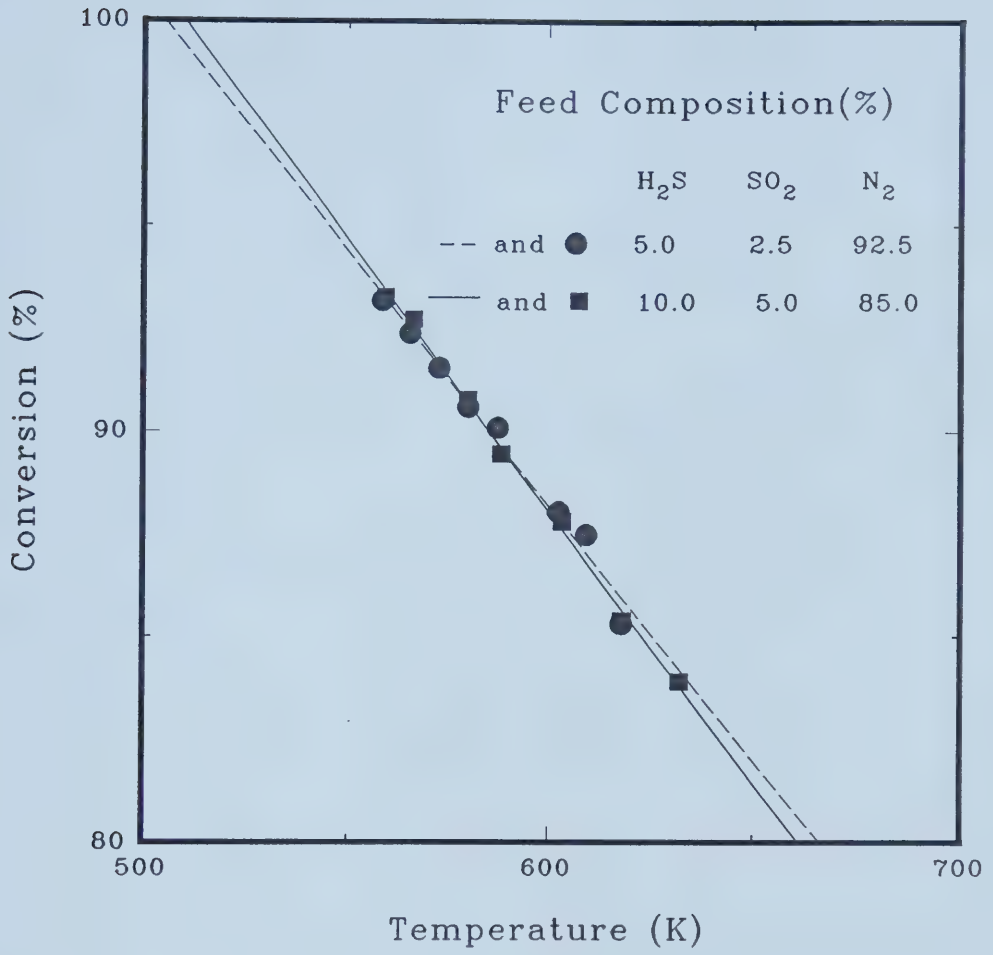


Figure 5-5 Conversion vs Temperature
For Different Feed Composition

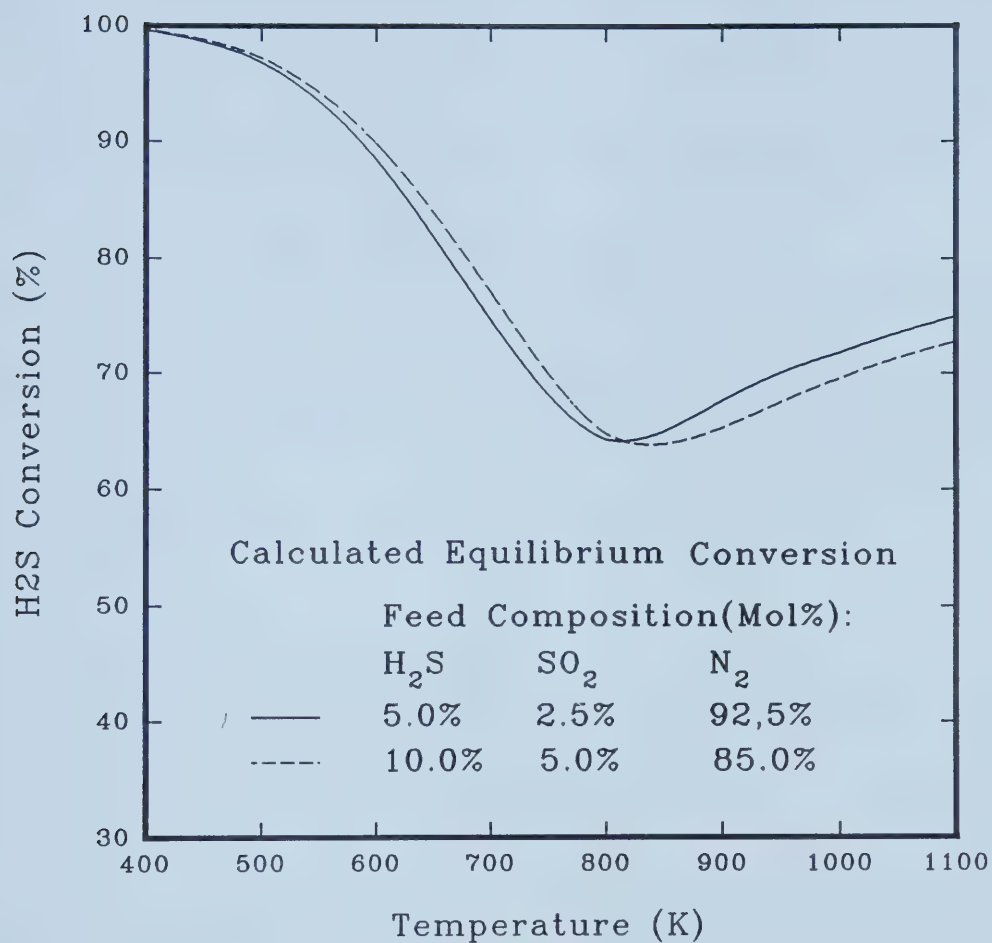


Figure 5-6 Calculated Equilibrium
Conversion As Function of Temperature
for Stoichiometric Feed

obtained. Firstly, when $T < 800$ K, the higher feed concentration results in a higher conversion, whereas, when $T > 800$ K, the reverse occurs. This corresponds to the reactions,



applying to the exothermic ($T < 800$ K) region and to the endothermic ($T > 800$ K) region, respectively, as shown in Figure 5-6. The same effect of feed composition upon conversion as predicted by thermodynamic calculation can be obtained via proper mathematical deduction (the detailed procedure is presented in Appendix E).

5.2.3 Non-stoichiometric Ratio of Feed Components

Four experimental runs were made to test the effect of a non-stoichiometric feed ratio of H_2S and SO_2 on conversion. Figure 5-7 shows that the conversion was dropping while the temperature was rising. From equation (1-3), it should be noted that the limiting H_2S conversion if SO_2 completely reacts in the 3:1 feed ratio of H_2S and SO_2 will be 66.7% because at least 1/3 of the H_2S remains unreacted.

5.3 THERMODYNAMIC ANALYSIS OF THE MODIFIED CLAUS REACTION

Reliable values for the thermodynamic properties of the species in reaction (1-3) are essential for accurate prediction of thermodynamic equilibrium conversions. Before the JANAF 3rd edition (1985) became available, accurate thermodynamic data were not available from a single source for all species in the Claus reaction system (in this study,

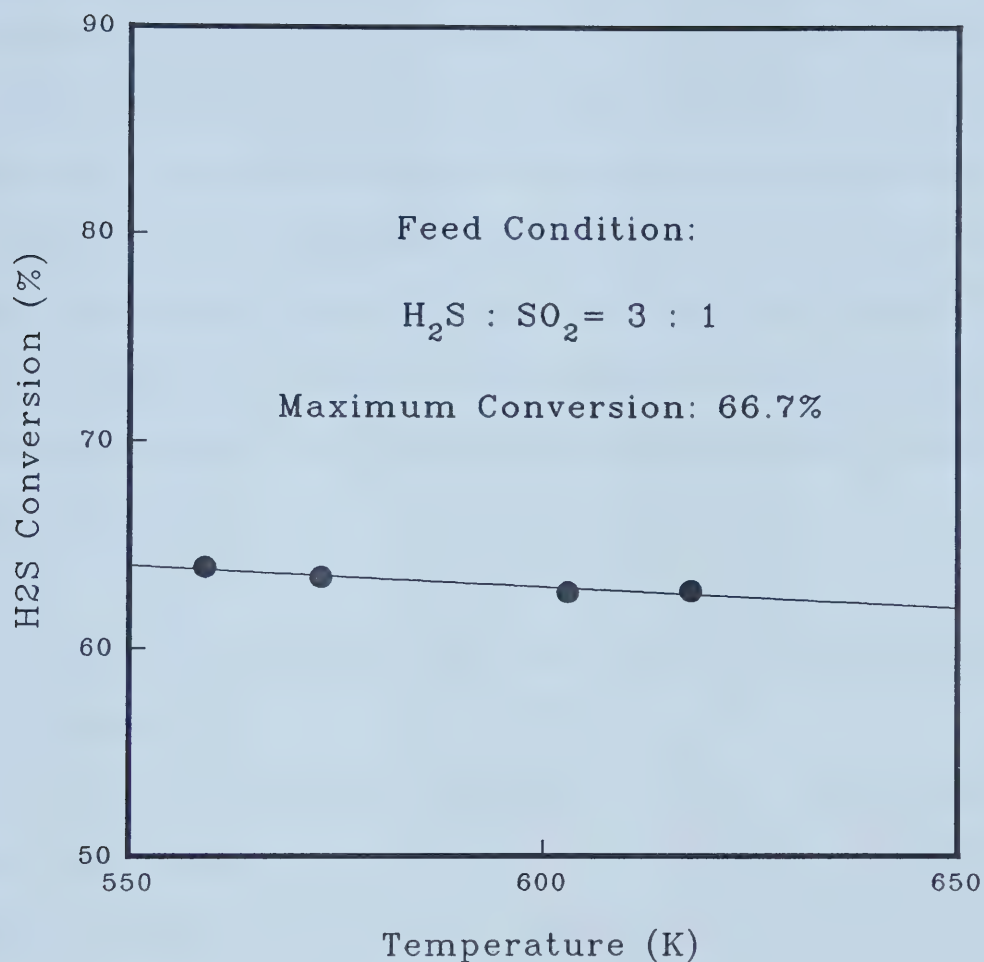


Figure 5-7 Experimental Equilibrium Conversion
As Function of Temperature for
Non-Stoichiometric Feed Ratio

the system comprises H_2S , SO_2 , H_2O , N_2 and S_n ($n=2, 3\cdots 8$). Sometimes researchers have combined thermodynamic data from different sources to predict the equilibrium conversion. If these different sources of thermodynamic properties are not consistent, their use could lead to inaccurate estimates of the thermodynamic equilibrium conversion. In this section, the use of thermodynamic properties from several sources is compared to predictions using properties from the most recent comprehensive JANAF 3rd edition. The various calculated values of the thermodynamic equilibrium conversion (based upon published thermodynamic data) will also be compared to the experimental conversions measured in this work.

5.3.1 Use of Combined Thermodynamic Properties from JANAF 2nd Edition and Kellogg

Before publication of the JANAF 3rd Edition (1985), no single complete listing of thermodynamic properties for all species present in the Claus system was available. Properties for each species listed in each of the editions of JANAF tables were developed by consolidating information from the many sources available at the time. These data were examined for consistency and accuracy, enabling JANAF to improve their reliability. Subsequently, each revised JANAF edition updated properties for listed species and included additional properties for not previously listed species.

In this section, the thermodynamic data for H_2S , SO_2 , H_2O , S_2 , S_8 and N_2 , which will be used, were obtained from the JANAF, 2nd Edition (1971). As to S_6 and S_7 , properties

which were not available in this edition, the free energy equation of Kellogg (1971) over the temperature range, 400-700 K, was used. The resulting free energy data for the 8 species are listed in Table 5-1. Thermodynamic equilibrium conversions were calculated using these data and plotted along with the experimental conversions in Figure 5-8.

5.3.2 Use of thermodynamic properties from JANAF 3rd Edition

In 1985, the JANAF, 3rd Edition, was published. This updated edition included the thermodynamic properties for all molecular species encountered in the Claus system including S_n ($n=2, 3...8$). Calculated thermodynamic equilibrium conversions, based upon the JANAF, 3rd Edition, are shown in Figure 5-9 along with the comparable experimental conversion data.

5.3.3 Evaluation of Thermodynamic Properties

To identify the more reliable group of the two sets of thermodynamic data mentioned in the above sections, the thermodynamically predicted and the experimental conversions were contrasted based upon the 5.0% H_2S stoichiometric feed composition. Both Figures 5-8 and 5-9 seem, at first glance, to show a slightly lower similar trend for the predicted thermodynamic conversions. However, a more careful examination of the comparison with experimental data based upon least-squares criterion described by Bauer (1960) shows that the JANAF 3rd edition properties predict a slightly better fit. The more detailed comparison is shown in Table 5-2 along with the standard deviation calculated from least-squares analysis. The JANAF 3rd Edition properties will be used in the

TABLE 5-1

GIBBS FREE ENERGY DATA FROM JANAF 2ND EDITION AND FROM KELLOGG

T(K)	H ₂ S	SO ₂	H ₂ O	S ₂	S ₆	S ₇	S ₈	N ₂
(kJ/Mol)								
400	-37.313	-301.026	-223.923	63.735	38.746	41.633	32.447	0.0
500	-40.150	-300.926	-219.078	49.396	27.472	29.282	22.096	0.0
600	-42.380	-300.369	-214.037	35.878	18.155	19.198	14.393	0.0
700	-44.091	-299.415	-208.844	22.117	10.689	11.260	9.184	0.0

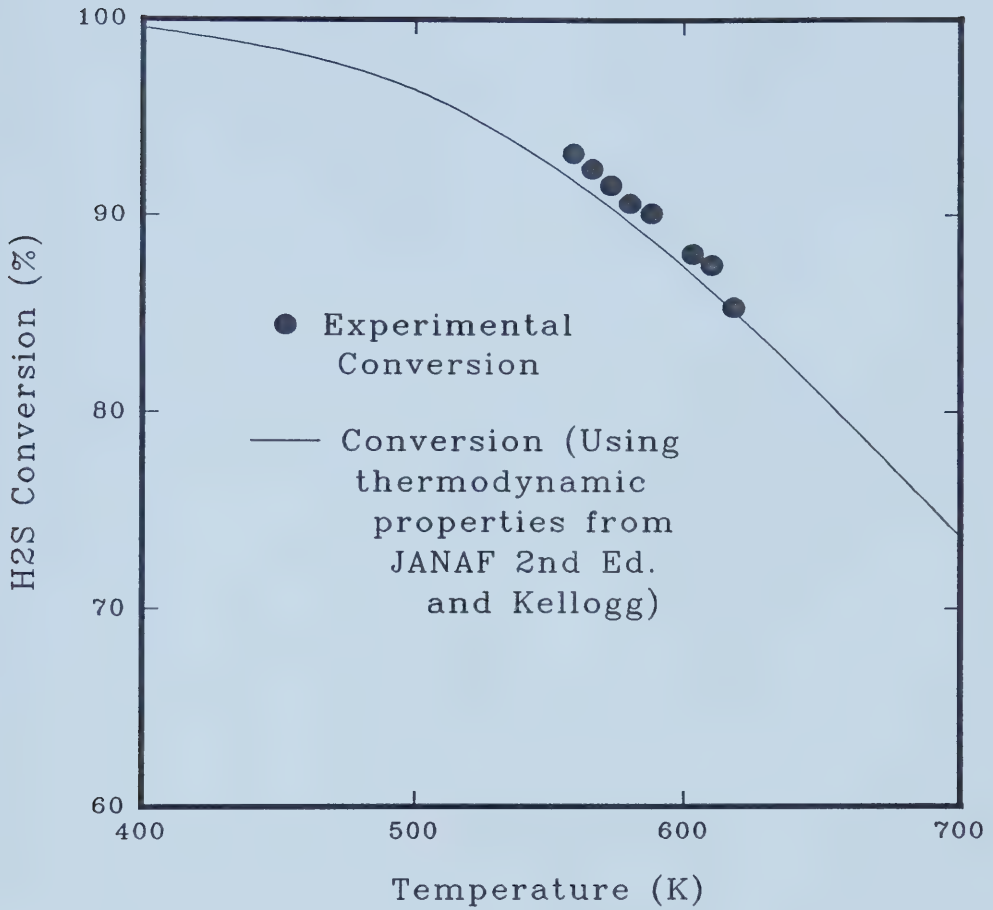


Figure 5-8 Comparison Between Experimental
and Thermodynamic Equilibrium Conversions
(Using thermodynamic properties from
JANAF 2nd Ed. and Kellogg)

Feed Composition:

H₂S: 5.0% SO₂: 2.5% N₂: 92.5%

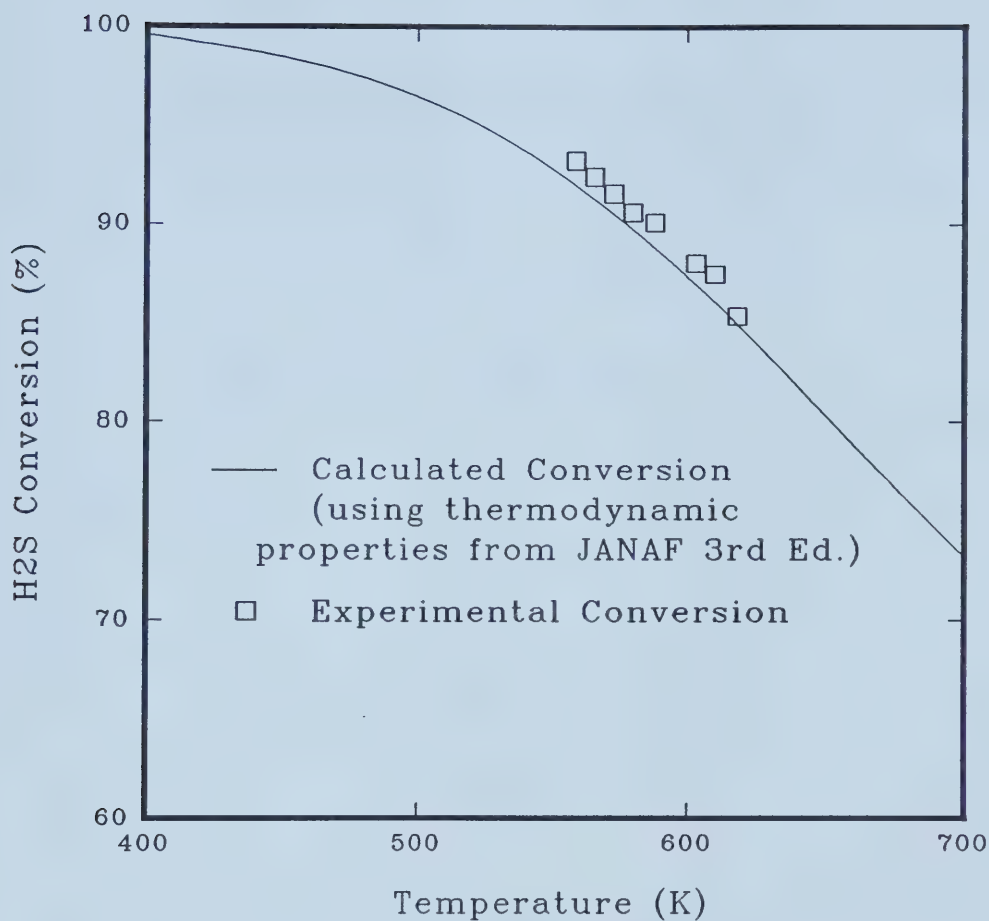


Figure 5-9 Comparison between Experimental
and Thermodynamic Equilibrium Conversions

(Using thermodynamic properties
from JANAF 3rd Ed.)

Feed Composition

H₂S: 5.0% SO₂: 2.5% N₂: 92.5%

TABLE 5-2

COMPARISON BETWEEN EXPERIMENTAL AND
THERMODYNAMICALLY PREDICTED EQUILIBRIUM CONVERSIONS

T(K)	EXP.CONV.(%)	JANAF 2ND	JANAF 3RD
		CONV.(%)	CONV.(%)
558.6	93.18	91.82	92.14
565.5	92.38	91.14	91.48
572.8	91.54	90.44	90.77
580.1	90.60	89.71	90.04
587.5	90.10	88.85	89.17
603.1	88.03	87.15	87.43
609.5	87.47	86.32	86.58
618.1	85.31	85.35	85.57
STANDARD DEVIATION:		1.137	0.835

remainder of this thesis.

The comparisons between experimental and equilibrium conversion shows again (Gamson and Elkins, 1953; Cho, 1975) that the experimental conversions are slightly greater than the corresponding predicted conversions.

5.3.4 Choice of an Appropriate Model for Sulphur Vapour

Figure 5-10 shows a comparison between experimental and thermodynamic equilibrium conversions for the modified Claus reaction when using different molecular models for sulphur vapour. For example, line 1 is based on a model containing S_2 , S_6 , S_7 , S_8 species. For line 6, only S_6 was assumed to be present in sulphur vapour. From the figure, it is evident that the single species models, S_6 or S_8 (lines 5 and 6), do not represent the experimental data well over the range of temperature plotted. It is clearly evident that models which do not include S_2 fail entirely to represent equilibrium conversion above 800 K. For the remaining four lines, it is difficult to decide which model of sulphur vapour fits best. Below 800 K, models 1, 2, 3 and 4, each of which contain S_6 and S_8 appear to fit best. The addition of S_7 seems to improve the prediction slightly. Within the limited experimental temperature studied, it is not possible to discriminate between models 1, 2, 3 and 4. Only the models tested containing S_2 , appear to be reliable overall based on the fact that the modified Claus reaction becomes endothermic at temperature above 800 K (Zhu and Bao, 1990). Again none of the models predict the experimental conversions accurately with model 1 being the most reliable.

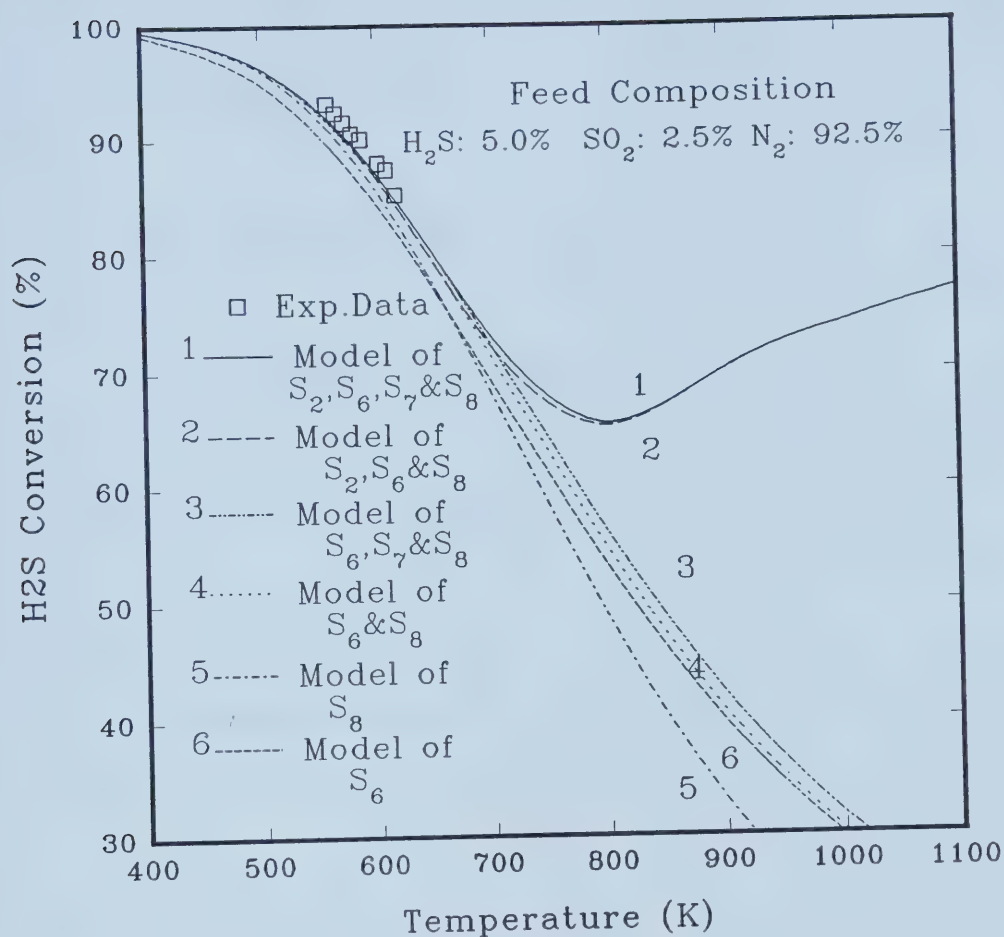


Figure 5-10 Comparison of Experimental and Predicted Equilibrium Conversion for Different Models of Sulphur Vapour

As will be shown, the experimental equilibrium conversions (in the absence of knowledge of the molecular species of sulphur present) may only be interpreted in terms of a single molecular species for sulphur.

5.4 DETERMINATION OF EQUILIBRIUM CONSTANTS BASED ON EXPERIMENTAL DATA AND A SULPHUR VAPOUR MODEL OF SINGLE MOLECULAR SPECIES

Computer program EES8 is listed (in Appendix A), enabling one to calculate the product distribution for the modified Claus reaction from the experimental conversions with the assumption of a single molecular species in sulphur vapour. The calculation sequence is rather simple. A material balance calculation using the experimental measured conversion, like that discussed in Chapter III, provides the number of sulphur gram-atoms formed in unit time. The total moles of sulphur vapour can then be calculated directly depending on which single species sulphur molecular model was used as the basis for the calculation. Once this is obtained, for the reaction,



with n fixed, the equilibrium constant, K_p , may be defined as follows,

$$K_p = \frac{\left[\frac{M_{\text{H}_2\text{O}}}{M_T} \right]^2 \left[\frac{M_{\text{S}_n}}{M_T} \right]^{\frac{3}{n}}}{\left[\frac{M_{\text{H}_2\text{S}}}{M_T} \right]^2 \left[\frac{M_{\text{SO}_2}}{M_T} \right]} P_T^{\frac{3}{n}-1} \quad (5-2)$$

Because K_p is a function of temperature, values of K_p were calculated for each reaction

temperature tested and, in turn, the consistency of the set of K_p values was checked for linearity by plotting according to the van't Hoff equation,

$$\ln K_p = A/T + B \quad (5-3)$$

Tables 5-3 to Table 5-6 show the product distribution for reaction 1-3 and the corresponding values of K_p calculated based upon a single sulphur species, S_2 , S_6 , S_7 or S_8 for the feed composition of H_2S : 5.0%, SO_2 : 2.5% and N_2 : 92.5%. A sample calculation to obtain K_p is given in Appendix C.

Figures 5-11 to Figure 5-14 present the plots of $\ln K_p$ versus $1/T$, according to the van't Hoff equation. For comparison, K_p values obtained using thermodynamic analysis via free energy minimization method were also plotted. In these Figures, the solid circles stand for experimental data with its linear regression shown by the dashed line. Similarly, the thermodynamic predictions using the free energy minimization method are shown by the solid line. From these Figures we can see that

- (1) Both experimental and thermodynamic data fit the van't Hoff equation well in terms of the relationship between $\ln K_p$ and $1/T$.
- (2) The experimentally determined K_p value is generally larger than the value predicted using thermodynamic properties, which implies that the experimental conversions are also larger than those predicted. The difference may be caused by: (a) improper assumption of a single sulphur molecular species in sulphur vapour; or, (b) the published thermodynamic properties used in the calculations still may not be accurate.

TABLE 5-3

PRODUCT DISTRIBUTION USING S2 ALONE

FEED COMPOSITION: H2S: 5.0% SO2:2.5% N2:92.5%

REACTION PRESSURE: 101.33 kPa

TEMP	H2S	SO2	H2O	S2	N2	Kp
(K)	(Mole Fraction)					
558.6	.00343	.00171	.0468	.0351	.913	717
565.5	.00383	.00191	.0464	.0348	.913	499
572.8	.00425	.00213	.0460	.0345	.913	353
580.1	.00472	.00236	.0455	.0341	.913	248
587.5	.00498	.00249	.0453	.0340	.913	208
603.1	.00602	.00301	.0442	.0332	.914	108
609.5	.00630	.00315	.0440	.0330	.914	93
618.1	.00739	.00369	.0429	.0322	.914	53

TABLE 5-4

PRODUCT DISTRIBUTION USING S6 ALONE

FEED COMPOSITION: H2S: 5.0% SO2: 2.5% N2: 92.5%

REACTION PRESSURE: 101.33 kPa

TEMP	H2S	SO2	H2O	S6	N2	Kp
(K)	(Mole Fraction)					
558.6	.00350	.00175	.0479	.0120	.935	11650
565.5	.00392	.00196	.0475	.0119	.935	8175
572.8	.00435	.00218	.0471	.0118	.935	5839
580.1	.00483	.00242	.0466	.0116	.935	4148
587.5	.00509	.00255	.0463	.0116	.934	3502
603.1	.00615	.00308	.0452	.0113	.934	1870
609.5	.00644	.00322	.0450	.0112	.934	1604
618.1	.00755	.00377	.0438	.0110	.934	935

TABLE 5-5

PRODUCT DISTRIBUTION USING S7 ALONEFEED COMPOSITION: H₂S: 5.0% SO₂: 2.5% N₂: 92.5%

REACTION PRESSURE: 101.33 kPa

TEMP (K)	H ₂ S (Mole Fraction)	SO ₂	H ₂ O	S7	N ₂	K _p
558.6	.00351	.00176	.0480	.0103	.936	14944
565.5	.00393	.00196	.0476	.0102	.936	10492
572.8	.00436	.00218	.0472	.0101	.936	7499
580.1	.00484	.00242	.0467	.0100	.936	5332
587.5	.00510	.00255	.0464	.00994	.936	4504
603.1	.00616	.00308	.0453	.00971	.936	2408
609.5	.00645	.00323	.0450	.00965	.936	2068
618.1	.00756	.00378	.0439	.00941	.935	1208

TABLE 5-6

PRODUCT DISTRIBUTION USING S8 ALONE

FEED COMPOSITION: H2S: 5.0% SO2: 2.5% N2: 92.5%

REACTION PRESSURE: 101.33 kPa

TEMP	H2S	SO2	H2O	S8	N2	Kp
(K)	(Mole Fraction)					
558.6	.00352	.00176	.0481	.00901	.938	18148
565.5	.00393	.00197	.0477	.00894	.938	12748
572.8	.00436	.00218	.0472	.00885	.937	9117
580.1	.00485	.00242	.0467	.00876	.937	6486
587.5	.00511	.00255	.0465	.00871	.937	5480
603.1	.00617	.00309	.0454	.00851	.937	2934
609.5	.00646	.00323	.0451	.00845	.937	2520
618.1	.00757	.00378	.0440	.00824	.936	1474

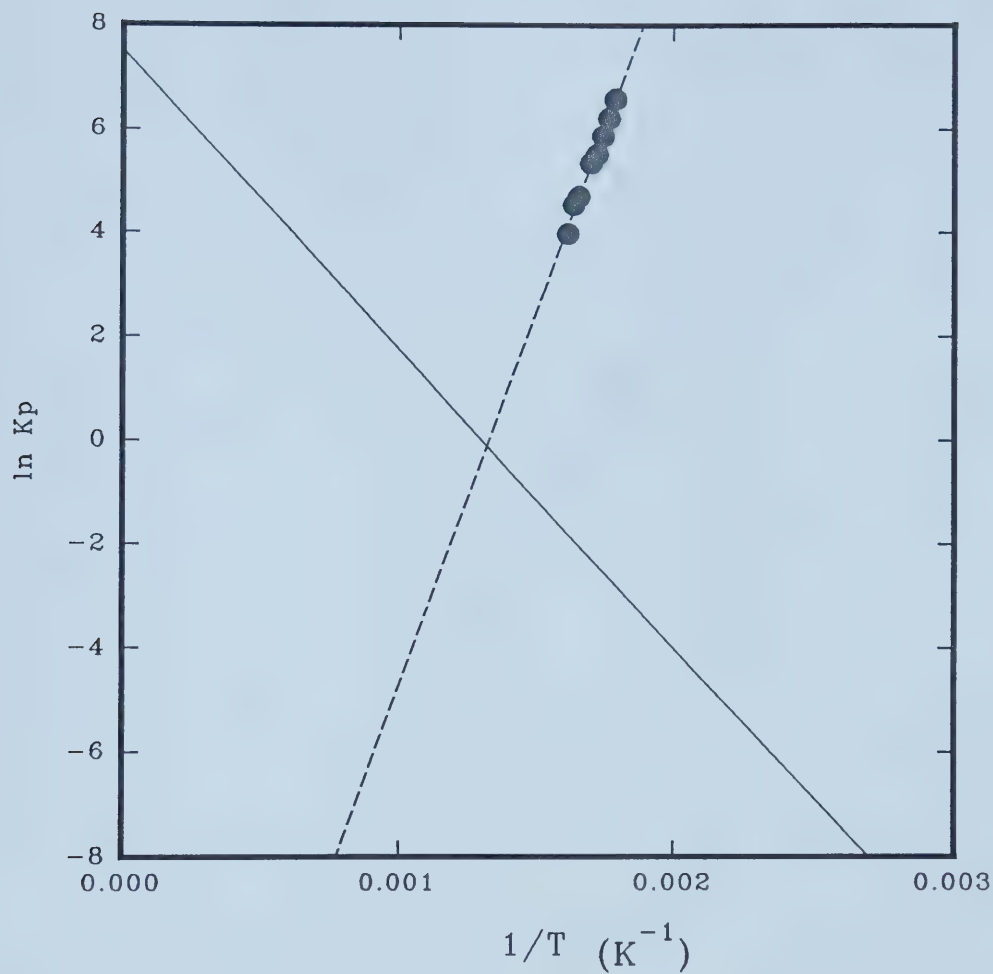


Figure 5-11 $\ln K_p$ vs $1/T$ for S_2 Model

● Experimental Data

— Thermodynamic Prediction

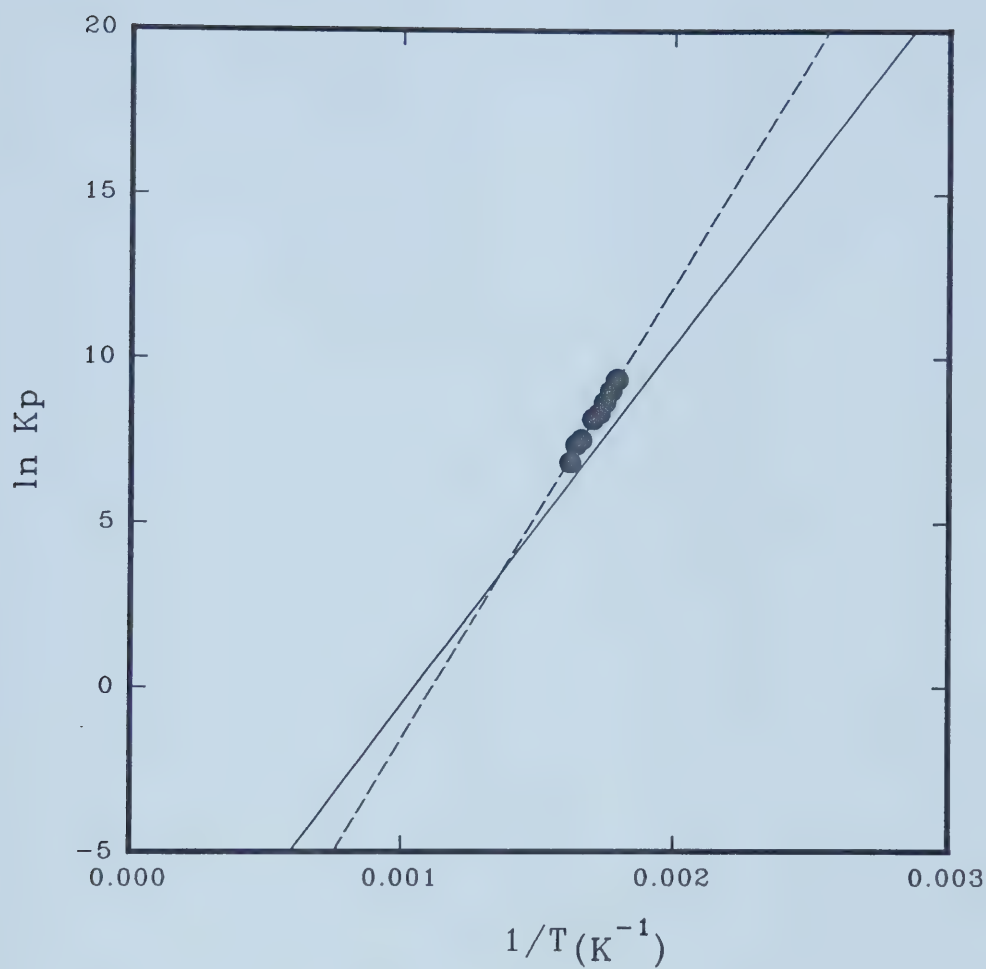


Figure 5-12 $\ln K_p$ vs $1/T$ for S_6 model

- Experimental Data
- Thermodynamic Prediction

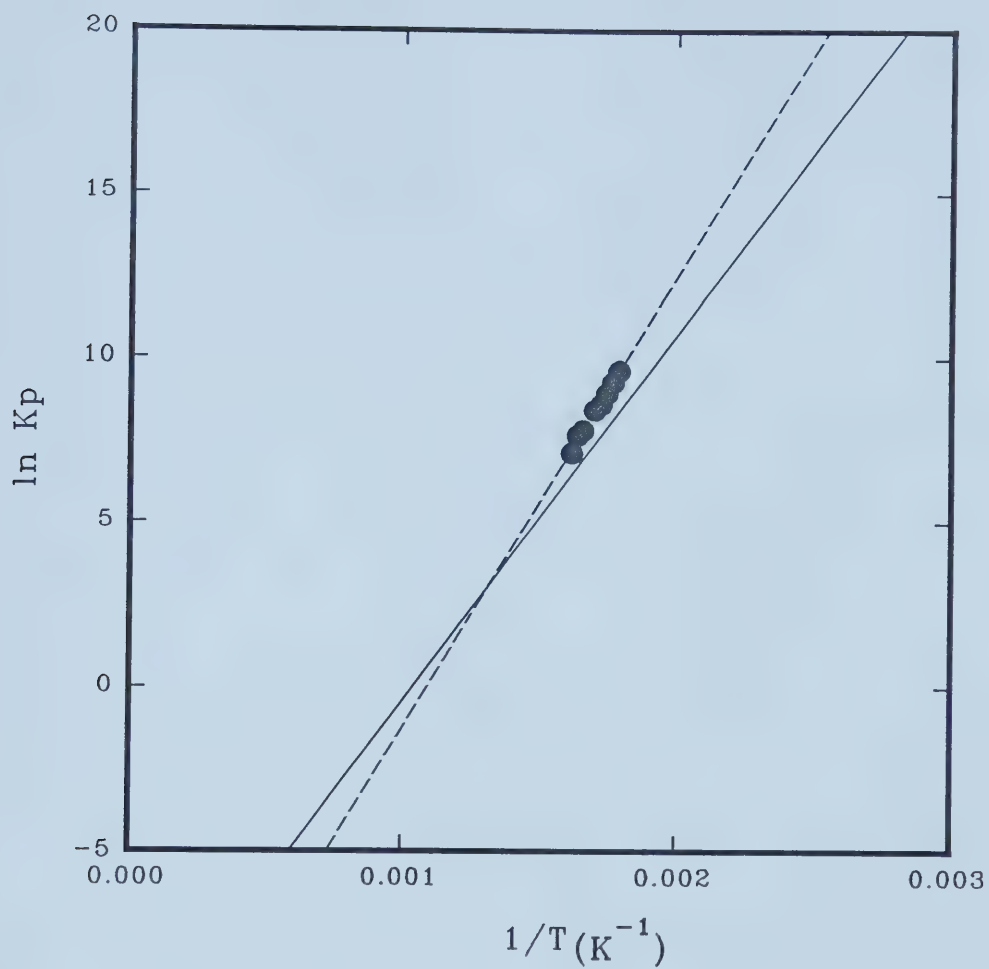


Figure 5-13 $\ln K_p$ vs $1/T$ for S_γ model

● Experimental Data
— Thermodynamic Prediction

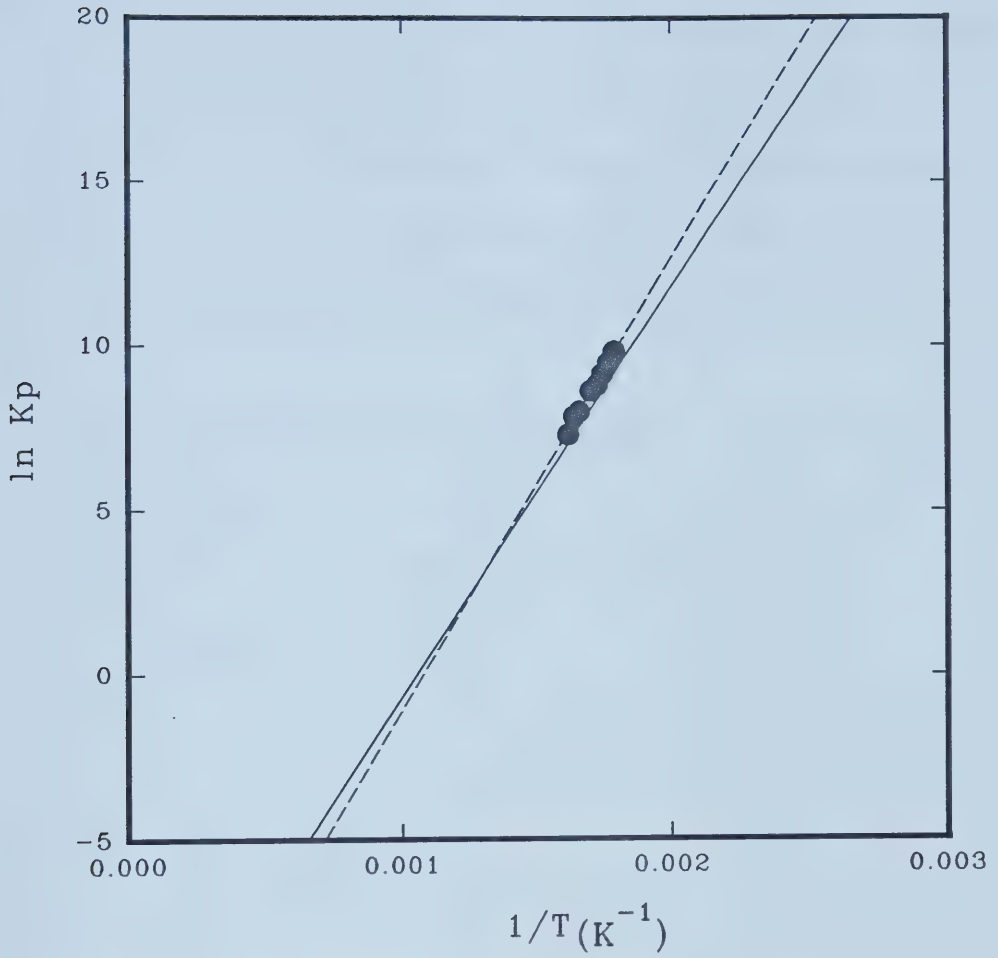


Figure 5-14 $\ln K_p$ vs $1/T$ for S_8 model

● Experimental Data

— Thermodynamic Prediction

(3) Of the four single sulphur molecular models examined, that with S_8 generates K_p values which fit closest to the thermodynamic predictions in the tested reaction temperature range. Alternatively, it may also mean that the single sulphur molecular species model is incorrect but that the assumption of S_8 introduces the least error. The dominance of S_8 in sulphur vapour over the experimental temperature range is evident here and also in Figure 5-10.

The resulting equilibrium constants for the reaction



in the temperature range from 560 to 620 K are given by

$$\ln K_{p1} = 13,750/T - 14.835 \quad (5-4)$$

with

$$K_{p1} = \frac{P_{S_8}^{\frac{3}{8}} P_{H_2O}^2}{P_{H_2S}^2 P_{SO_2}} \quad (3-21)$$

5.5 EXAMINATION OF EXPERIMENTAL EQUILIBRIUM CONSTANT

5.5.1 Equilibrium Limits from Experimental Work

The main goal of this experimental work was to contribute information which could be used to predict equilibrium limits at various conditions for the modified Claus reaction system. The assumptions of either S_2 or S_8 alone to comprise sulphur vapour provided upper and lower limits, respectively, for predicting the total equivalent moles of sulphur in the product mixture, and correspondingly, limiting values of the equilibrium constant.

In section 5.4 the relationships between K_p and T for sulphur vapour models containing S_2 or S_8 were shown. The calculated results are presented in Table 5-7. The relationships between $\ln K_p$ and $1/T$ are exhibited in Figure 5-15. The region bordered by dashed and dotted lines in the figure represents the area within which the relationship of $\ln K_p$ vs $1/T$ for modified Claus reaction should lie when using single molecular species models of sulphur vapour.

5.5.2 Equilibrium Prediction Using Experimental Conversions and Thermodynamically Determined Average Sulphur Atomic Number

In the preceding section, the calculation of equilibrium constants from the experimental conversion was limited to single molecular species in sulphur vapour. We showed in 5.3.3 that the thermodynamically determined equilibrium conversions which used the sulphur vapour model containing S_2 , S_6 , S_7 and S_8 and thermodynamic properties from the JANAF 3rd edition were most consistent with the experimental results. This suggests that thermodynamically calculated product distributions may be used with the experimental conversion data to estimate equilibrium constants for the modified Claus reaction,



$$K_p = \frac{\left[\frac{M_{H_2O}}{M_T} \right]^2 \left[\frac{M_{S_x}}{M_T} \right]^{\frac{3}{x}}}{\left[\frac{M_{H_2S}}{M_T} \right]^2 \left[\frac{M_{SO_2}}{M_T} \right]} P_T^{\frac{3}{x}-1} \quad (5-6)$$

TABLE 5-7

EQUILIBRIUM CONSTANT WITH MODEL OF S₂ OR S₈

TEMP (K)	K _p	
	Model S ₂	Model S ₈
558.6	717	18148
565.5	499	12749
572.8	353	9117
580.1	248	6486
587.5	208	5480
603.1	109	2934
609.5	93	2520
618.1	53	1474

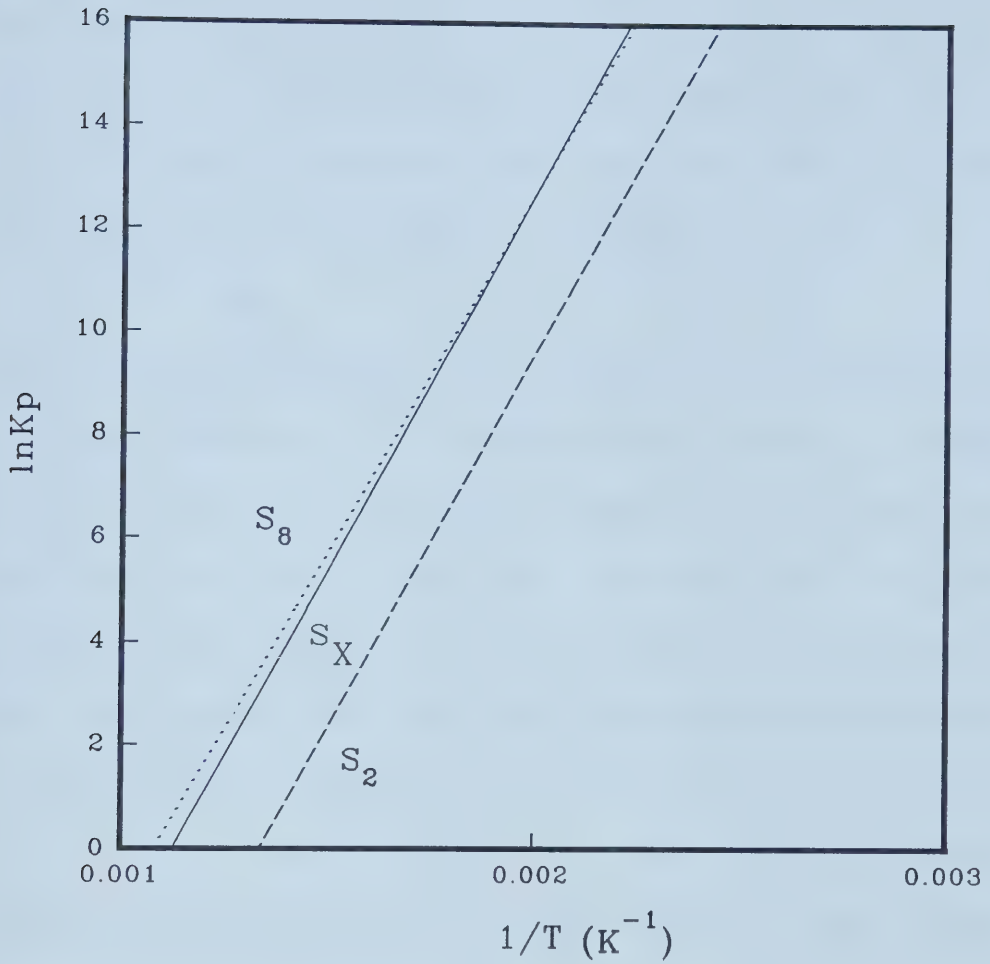


Figure 5-15 Equilibrium Limits

from Experimental Work

(Solid line represents the result by using
average sulphur atomic number)

by introducing an average sulphur atomic number, X . To carry out this approach, the thermodynamic equilibrium conversion is first used to calculate the total gram-atom number (N_{sg}) for sulphur and then the equilibrium product distribution of S_2 , S_6 , S_7 and S_8 is used to calculate the total moles of sulphur vapour (M_{Ts}). The average sulphur atomic number, X , would then be obtained from the equation,

$$X = N_{sg}/M_{Ts} \quad (5-7)$$

Second, by using the experimental conversion data (instead of thermodynamic conversion ones) and the calculated value of X , K_p is then obtained by following the procedure described in section 5.4 for the determination of equilibrium constants based upon a sulphur vapour model containing a single molecular species (for a sample calculation of X , please refer to the Appendix C). This method has some merit: (1) the use of an average atomic number, X , should provide an improved K_p compared to that obtained from using a single species, namely, S_2 or S_6 or S_7 or S_8 ; (2) we can probably correct, to some extent, the thermodynamically predicted conversions by using experimental conversion data; (3) it provides a relatively simple but improved method to predict equilibrium performance for the modified Claus reaction.

Table 5-8 shows an average atomic number and associated equilibrium constant using equation (5-6) under the reaction conditions specified in the table. The relationship of $\ln K_p$ vs $1/T$ is also presented in Figure 5-15 by the solid line.

TABLE 5-8
COMPARISON OF K_p VALUES

T	X	K_{p_x}
558.6	7.231	15695
565.5	7.187	10921
572.8	7.140	7729
580.1	7.089	5437
587.5	7.025	4529
603.1	6.889	2349
609.5	6.814	1982
618.1	6.719	1132

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

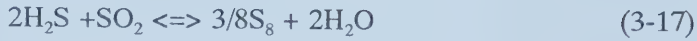
Feed composition changes at constant 2:1 stoichiometric ratio for $\text{H}_2\text{S}/\text{SO}_2$ in the range (from 5.0% to 10.0% of H_2S) tested, did not affect the experimental conversions significantly at the above converter temperatures and pressure of about 101.33 kPa. Within the error limits calculated for the various experimental conversions, the experimental data do not conflict with the predicted effect of composition upon conversion. The experimental data also appear to be insensitive to changes in feed composition ranging from 5 to 10% H_2S .

With the present experimental equipment, equilibrium conversions could be reached using a space velocity of about 360 h^{-1} and after a run duration of 3 hours.

The thermodynamically predicted equilibrium conversions (by means of a free energy minimization method based on thermodynamic properties from the JANAF, 3rd edition (1985) for each species in the product mixture) are all slightly different and generally lower than the experimental conversions if sulphur vapour models such as $\text{S}_2\text{-S}_6\text{-S}_7\text{-S}_8$, $\text{S}_2\text{-S}_6\text{-S}_8$, $\text{S}_6\text{-S}_7\text{-S}_8$ or $\text{S}_6\text{-S}_8$ are assumed. The model of sulphur vapour, $\text{S}_2\text{-S}_6\text{-S}_7\text{-S}_8$, provided the closest fit to the limited experimental conversion data and predicts slightly lower equilibrium conversions.

Using the experimental equilibrium conversion data, it was possible to calculate values for K_p only in terms of a single molecular species for sulphur vapour. The use of S_8

provided better agreement than from the use of S_7 or S_6 . The equilibrium constant for the reaction based on S_8 ,



over the temperature range from 560 to 620 K is given by

$$\ln K_{p1} = 13,750/T - 14.835 \quad (5-4)$$

6.2 RECOMMENDATIONS

6.2.1 Experimental systems

6.2.1.1 Feed system

Because of the corrosiveness of H_2S and SO_2 gases, Teflon packing and seals were necessary in the flow controllers. After each experimental run, complete purging with N_2 is highly recommended. Furthermore, since effects of H_2S and SO_2 on packing and seals may cause deformation by swelling, which would in turn affect the size of the actual opening in the controller, frequent checks of the calibrations of these controllers are necessary to maintain their accuracy.

6.2.1.2 Reaction system

Using a minimum reactor length should reduce the pressure drop along the reactor. According to Cho (1975), at space velocity of 1000 h^{-1} and pressure of 101.33 kPa, the equilibrium conversion could be reached after 80 cm of catalyst bed length. This suggests that use of the current space velocity (364 h^{-1}) alone with 31 cm long catalyst bed should enable generation of equilibrium conversion data. This modification of the laboratory

reactor to a shorter length, could enable two reactors in series but in different ovens to be used in each run.

The capacity of the current sulphur condenser to handle the product stream was limited because the outlet line of the condenser was quite often plugged with solid sulphur contained in the condensed stream leaving the condenser. This indicated that condensed sulphur vapour was not completely removed in the condenser and suggested that additional cooling to solid sulphur was resulting. A more efficient sulphur demister should be incorporated.

6.2.1.3 Analysis system

Some modification are needed in the GC analysis system: first, the sulphur traps must be carefully designed and manufactured, both in size and length, since these factors may affect the shape and separation of each component peak; second, the quality of H_2O separation in the GC has to be improved to enable conversions to be calculated independently via SO_2 consumption or H_2O production. This would enable the accuracy of conversions based on H_2S consumption to be checked.

6.2.2 Experiments

To obtain more extensive information about the modified Claus reaction, the experimental temperature range should be extended. In addition, the use of more concentrated $\text{H}_2\text{S}/\text{SO}_2$ mixtures would provide more accurate GC analysis and corresponding equilibrium

composition measurements. The resulting calculated conversions should be more accurate. Since H_2O vapour is a product whose concentration may also influence the reversible $\text{H}_2\text{S}/\text{SO}_2$ reaction, the effect of H_2O vapour upon conversion also merits study. For a more complete analysis of this reaction system, the effects of pressure, a wider range of feed compositions and non-stoichiometric ratios of $\text{H}_2\text{S}/\text{SO}_2$ in the feed should also be considered in future work.

6.2.3 Possibility of Independently Measuring the Total Moles of Sulphur

Vapour

Figure 6-1 suggests an experiment which could provide additional independent data pertinent to the calculation of the total moles of sulphur vapour. A special insulated vessel of known volume connected to the reaction oven outlet is first evacuated and then maintained at the reaction outlet temperature. The product mixture is then introduced into the container until a steady product composition state has been reached. After, isolating the vessel, knowing the initial pressure, temperature (P_1 and T_1) and the volume (V) within the vessel should enable us to calculate the total moles in the vessel by means of the ideal gas law. Next, the vessel is cooled carefully to T_2 ($100^\circ\text{C} < T_2 < 120^\circ\text{C}$) to condense the sulphur but leave the H_2O in the vapour phase. Finally, measure pressure P_2 at T_2 and calculate total moles present after the sulphur has condensed. The difference between the two numbers of total moles present should provide the total moles of sulphur vapour originally present in the vessel. The problem described in section 3.2.2 could then be solved in terms of a two-molecular-species model of sulphur vapour.

To examine sulphur vapour models containing more than two molecular species, additional independent experimental information is needed. This would necessitate use of a mass spectrometer providing that sulphur vapour could be introduced without detriment to the MS instrument.

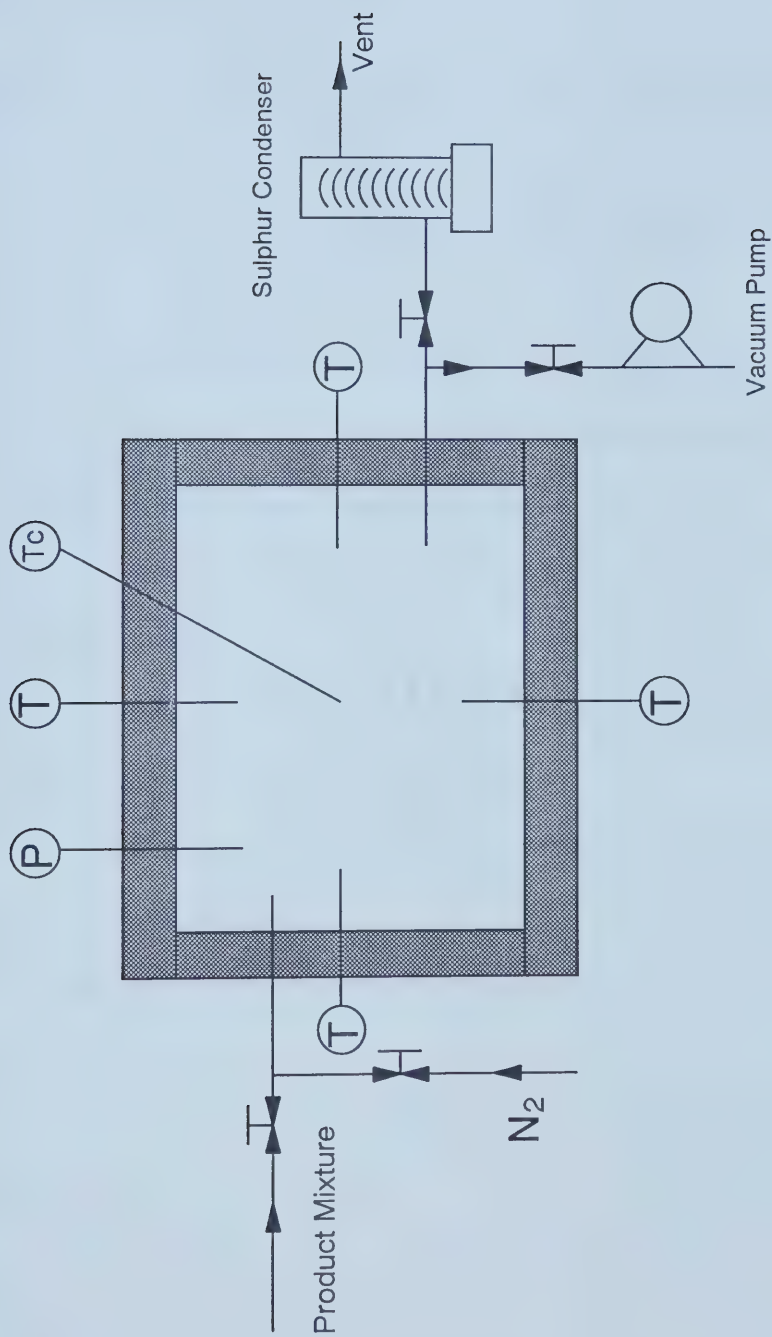


Figure 6-1 Measurement of Total Moles of Sulphur Vapour

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APPENDIX A

COMPUTER PROGRAMS

-----FEMP-----

THIS IS A PROGRAM DESIGNED TO ESTIMATE THERMODYNAMIC
EQUILIBRIUM DISTRIBUTION FOR THE REACTION SYSTEM OF SO₂/H₂S/N₂
THE COMPOUNDS TO BE CONSIDERED IN THE SYSTEM INCLUDE:

H₂S SO₂ H₂O S₂ S₆ S₇ S₈ N₂ (8)

```
REAL SNAM(20), FRE(8,8), X(8), GA(20,20), GB(20), GX(20),
&C(20),
&DEN(8), F(20), A(8,4), Y(20), B(20), FRC(20), NG1(20),
&OTPT(23,8)
&ANAM(8),DES(20),IPVT(20),WORK(20),XSTOR(8),T(8)
INTEGER NCOP,NCOPY
OPEN(UNIT=7,FILE='b:-R')
```

```
WRITE(6,*)'COEF. FOR FREE ENERGY EXPRESSION'
H2S SO2 H2O S2 S6 S7 S8 N2 (8)
DATA T /400,500,600,700,800,900,1000,1100/
DATA PRESS/1.0/
DATA FRE/-37.343,-300.971,-223.901,63.371,38.152,41.399,
* 32.003,0.0,
* -40.179, -300.871,-219.051,49.019,27.426,29.310,
* 21.636,0.0,
* -42.399, -300.305,-214.007,35.511,18.838,19.665,
* 14.009,0.0,
* -44.201, -299.444,-208.812,22.562,11.592,11.543,
* 8.078,0.0,
* -45.694, -298.370,-203.496,10.033, 5.320, 4.522,
* 3.368,0.0,
* -45.870, -296.051,-198.083,0.0 , 6.293, 5.919,
* 8.246,0.0,
* -40.984, -288.725,-192.59, 0.0 ,37.144,42.144,
* 52.900,0.0,
* -36.066, -281.409,-187.033,0.0 ,67.806,78.117,
* 97.243,0.0/
```

```
H2S SO2 H2O S2 S6 S7 S8 N2 (8)
DATA A/2.0,0.0,2.0,0.0,0.0,0.0,0.0,0.0
$ ,1.0,1.0,0.0,2.0,6.0,7.0,8.0,0.0
$ ,0.0,2.0,1.0,0.0,0.0,0.0,0.0,0.0
$ ,0.0,0.0,0.0,0.0,0.0,0.0,0.0,2.0/
```

```
WRITE(6,*)'ENTER HOW MANY FEED CONDITIONS, EPS, ITER'
READ(5,*)NCASE,EPS,ITER
DO 205 ICASE=1,NCASE
```



```

WRITE(6,*)'ENTER FEED COMPOSITIONS'
WRITE(7,*)'ENTER FEED COMPOSITIONS'

WRITE(6,*)'H2S SO2 H2O  S2 S6 S7 S8 N2'
WRITE(7,*)'H2S SO2 H2O  S2 S6 S7 S8 N2'
READ(5,*)X
WRITE(6,*)X
WRITE(7,*)X
WRITE(6,*)'ENTER H2S VOLUMN IN FEED'
READ(5,*)H2S
WRITE(6,*)'ELEMENT NO (M) ,COMPOUND NO (N)'
READ(5,*)M,N
DO 5000 I=1,N
5000 XSTOR(I)=X(I)
    N1=N+2
    DO 43 NCOP=1,NCOPY
        WRITE(6,6)
        WRITE(7,6)
6    FORMAT('1',///,39X,'DATA ECHO CHECK',//37X,'MASS',
$' BALANCE MATRIX'//25X,'MOLECULAR',2X,' H  S  O  N')
        WRITE(6,65)
        WRITE(7,65)
65    FORMAT(25X,'SPECIES')
        DO 66 I=1,N
            WRITE(6,40) (A(I,J),J=1,M),X(I)
66    WRITE(7,40) (A(I,J),J=1,M),X(I)
40    FORMAT(27X,10X,10(F5.2,1X)/)
43    CONTINUE
        CALL DISTR(X,Y,B,N,M,A)
        JBI=2
        DO 205 ICAT=1,4

            DO 10 NC=1,8
                IF (T(NC)-.01) 206,206,13
13    OTPT(1,NC)=T(NC)
                OTPT(2,NC)=PRESS

            DO 12 I=1,N
                NG1(I)=0
12    C(I)=FRE(I,NC)*1000/8.314/T(NC)+ALOG(PRESS)
            DO 35 JB=1,JBI

                DO 14 ITE=1,ITER
                    CALL FREN(Y,C,F,YBAR,N,NG1)

```



```

MG=M+1
CALL GSET(A,Y,GA,GB,B,F,M,MG,N)

```

```

NDIM=20
CALL DECOMP(NDIM,MG,GA,COND,IPVT,WORK)
WRITE(6,3)COND
CONDP1=COND+1
IF(CONDP1.EQ.COND)WRITE(6,4)
IF(CONDP1.EQ.COND)WRITE(7,4)
4 FORMAT(40H MATRIX IS SINGULAR TO WORKING PRECISION)
IF(CONDP1.EQ.COND)STOP

```

```

CALL SOLVE(NDIM,MG,GA,GB,IPVT)
DO 18 I=1,N
  IF (NG1(I)) 19,19,18
19 X(I)=-Y(I)*((C(I)+ALOG(Y(I)/YBAR))-GB(1))
  DO 21 J=1,M
    IG=J+1
21 X(I)=X(I)+GB(IG)*A(I,J)*Y(I)
18 CONTINUE
  QUIT=1.

```

```

  DO 22 I=1, N
    IF (NG1(I)) 23,23,22
23 TEST=(XSTOR(I)-X(I))/X(I)
    IF (ABS(TEST)-EPS) 22,22,24
24 QUIT=-1.
22 CONTINUE
  DO 4000 I=1,N
4000 XSTOR(I)=X(I)
    IF(QUIT) 25,25,26
25 CALL NEZE(X,Y,N,NG1)
    DO 27 I=1,N
27 Y(I)=X(I)
14 CONTINUE
  WRITE(6,3)COND
  3 FORMAT(6H COND=,E15.5)
26 DO 32 I=1,N
  NG1(I)=0
  IF (X(I)) 33,33,34
34 Y(I)=X(I)
  GO TO 32
33 Y(I)=0.000001
32 CONTINUE

```



```

35 CONTINUE
   DEN(NC)=0.0
   DO 150 I=1,N
150 DEN(NC)=DEN(NC)+Y(I)
   DO 151 I=1,N
151 FRC(I)=Y(I)/DEN(NC)*100
   DO 36 I=3,N1
   II=I-2
36 OTPT(I,NC)=FRC(II)
   JBI=1
   NCP=N+3
   OTPT(NCP,NC)=(H2S-X(1))/H2S
   DO 37 NJ=4,2*N+1
   OTPT(N+NJ,NC)=X(NJ)/(H2S-X(1))
37 CONTINUE
   10 WRITE(6,*)'ITERATIONS =' ,ITE
   START TO PRINT OUT THE RESULTS
206 NPT=NC-1
   NCOPY=1
   DO 208 NCOP=1,NCOPY
   WRITE(6,300)PRESS
   WRITE(7,300)PRESS
300 FORMAT('PRESS(BAR)=' ,F5.2)
   WRITE(6,81)
   WRITE(7,81)
81  FORMAT(2X,'TEMP(K)', 'H2S SO2 H2O S2 S6 S7 S8 N2')
   DO 666 J=1,NPT
   WRITE(6,82)OTPT(1,J),(OTPT(I,J),I=3,N1)
666 WRITE(7,82)OTPT(1,J),(OTPT(I,J),I=3,N1)
   WRITE(6,83)
   WRITE(7,83)
83  FORMAT(2X,'TEMP(K)', 'Conv% S2sel S6sel S8sel F(m3/h)')
   DO 667 J=1,NPT
   WRITE(6,82)OTPT(1,J),(OTPT(I,J),I=N+3,2*N+1)
667 WRITE(7,82)OTPT(1,J),(OTPT(I,J),I=N+3,2*N+1)
   82 FORMAT(2X,F6.1,13(F8.4,1X))
208 CONTINUE
205 CONTINUE
   STOP
   END

```

```

SUBROUTINE DISTR(X,Y,B,N,M,A)
INTEGER M,N

```



```

      REAL X(20),Y(20),B(20),A(N,M)
      DO 1 I=1,N
      IF(X(I)) 2,2,1
2  X(I)=0.0000001
1  Y(I)=X(I)
      DO 3 J=1,M
      B(J)=0.0
      DO 3 I=1,N
3  B(J)=B(J)+A(I,J)*Y(I)
      RETURN
      END

```

SUBROUTINE FREN(Y,C,F,YBAR,N,NG1)

```

      REAL Y(20),C(20),F(20),NG1(20)
      YBAR=0.0
      DO 1 I=1,N
1  YBAR=YBAR+Y(I)
      DO 2 I=1,N
      IF(NG1(I)) 3,3,4
3  F(I)=Y(I)*(C(I)+ALOG(Y(I)/YBAR))
      GO TO 2
4  F(I)=0.0
2  CONTINUE
      RETURN
      END

```

SUBROUTINE GSET(A,Y,GA,GB,B,F,M,MG,N)

```

      INTEGER M,N
      REAL R(20,20),A(N,M),Y(20),GA(20,20),GB(20),B(20),F(20)
      DO 1 K=1,M
      DO 1 J=1,K
      R(J,K)=0.0
      DO 2 I=1,N
2  R(J,K)=R(J,K)+A(I,J)*A(I,K)*Y(I)
1  R(K,J)=R(J,K)
      DO 3 I=1,MG
      DO 3 J=1,MG
3  GA(I,J)=0.0
      DO 4 IG=1,M
      DO 5 I=1,N

```



```

5  GA(IG,1)=GA(IG,1)+A(I,IG)*Y(I)
   DO 9 J=1,M
     JG=J+1
9  GA(IG,JG)=R(IG,J)
   JG=IG+1
   IGG=M+1
4  GA(IGG,JG)=GA(IG,1)
   DO 10 J=1,M
     GB(J)=B(J)
     DO 10 I=1,N
10  GB(J)=GB(J)+A(I,J)*F(I)
     JGB=M+1
     GB(JGB)=0.0
     DO 11 I=1,N
11  GB(JGB)=GB(JGB)+F(I)
   RETURN
   END

```

SUBROUTINE DECOMP(NDIM,N,A,COND,IPVT,WORK)

```

INTEGER NDIM,N
REAL A(NDIM,N),COND,WORK(N)
INTEGER IPVT(N)

```

DECOMPOSES A REAL MATRIX BY GAUSSIAN ELIMINATION
AND ESTIMATES THE CONDITION OF THE MATRIX.

USE SOLVE TO COMPUTE SOLUTIONS TO LINEAR SYSTEMS.

INPUT:

NDIM =DECLARED ROW DIMENSION OF THE ARRAY CONTAINING A.

N =ORDER OF THE MATRIX

A =MATRIX TO BE TRIANGULARIZED.

OUTPUT:

A CONTAINS AN UPPER TRIANGULAR MATRIX U AND A PERMUTED
VERSION OF A LOWER TRIANGULAR MATRIX I-L SO THAT
(PERMUTATION MATRIX)*A=L*U

COND=AN ESTIMATE OF THE CONDITION OF A.
 FOR THE LINEAR SYSTEM $A \cdot X = B$, CHANGES IN A AND B
 MAY CAUSE CHANGES COND TIMES AS LARGE IN X.
 IF $COND + 1.0 \cdot EQ. COND$, A IS SINGULAR TO WORKING
 PRECISION. COND IS SET TO $1.0E+32$ IF EXACT
 SINGULARITY IS DETECTED.

IPVT=THE PLOT VECTOR.

IPVT(K)=THE INDEX OF THE K-TH PIVOT ROW.

IPVT(N)= $(-1)^{**}(\text{NUMBER OF INTERCHANGES})$

WORK SPACE: THE VECTOR MUST BE DECLARED AND INCLUDED
 IN THE CALL. ITS INPUT CONTENTS ARE IGNORED.
 ITS OUTPUT CONTENTS ARE USUALLY UNIMPORTANT.

THE DETERMINANT OF A CAN BE OBTAINED ON OUTPUT BY
 $DET(A) = IPVT(N) \cdot A(1,1) \cdot A(2,2) \cdot \dots \cdot A(N,N)$.

REAL EK,T,ANORM,YNORM,ZNORM
 INTEGER NM1,I,J,K,KP1,KB,KM1,M

IPVT(N)=1
 IF(N.EQ.1)GOTO 80
 NM1=N-1

COMPUTE 1-NORM OF A

ANORM=0.0
 DO 10 J=1,N
 T=0.0
 DO 5 I=1,N
 T=T+ABS(A(I,J))
 5 CONTINUE
 IF(T.GT.ANORM)ANORM=T
 10 CONTINUE

GUASSIAN ELIMINATION WITH PARTIAL PIVOTING

DO 35 K=1,NM1
 KP1=K+1

 FIND PIVOT
 M=K
 DO 15 I=KP1,N


```

      IF(ABS(A(I,K)).GT.ABS(A(M,K)))M=I
15  CONTINUE
      IPVT(K)=M
      IF(M.NE.K)IPVT(N)=-IPVT(N)
      T=A(M,K)
      A(M,K)=A(K,K)
      A(K,K)=T

```

SKIP STEP IF PIVOT IS ZERO

```

      IF(T.EQ.0.0)GOTO 35

```

COMPUTE MULTIPLIERS

```

      DO 20 I=KP1,N
        A(I,K)=-A(I,K)/T
20  CONTINUE

```

INTERCHANGE AND ELIMINATE BY COLUMNS

```

      DO 30 J=KP1,N
        T=A(M,J)
        A(M,J)=A(K,J)
        A(K,J)=T
        IF(T.EQ.0.0)GOTO 30
        DO 25 I=KP1,N
          A(I,J)=A(I,J)+A(I,K)*T
25  CONTINUE
30  CONTINUE
35 CONTINUE

```

COND=(1-NORM OF A)*(AN ESTIMATE OF 1-NORM OF A-INVERSE)
 ESTIMATE OBRAINED BY ONE STEP OF INVERSE ITERARION FOR THE
 SMALL SINGULAR VECTOR. THIS INVOLVES SOLVING TWO SYSTEMS
 OF EQUATIONS, (A-TRANPOSE)*Y=E AND A*Z=Y WHERE E
 IS A VECTOR OF +1 OF -1 CHOSEN TO CAUSE GROWTH IN Y.
 ESTIMATE=(1-NORM OF Z)/(1-NORM OF Y)

SOLVE (A-TRANPOSE)*Y=E

```

      DO 50 K=1,N
      T =0.0
      IF(K.EQ.1)GOTO 45
      KM1=K-1

```



```

      DO 40 I=1,KM1
        T=T+A(I,K)*WORK(I)
40  CONTINUE
45  EK=1.0
      IF(T.LT.0.0)EK=-1.0
      IF(A(K,K).EQ.0.0)GOTO 90
      WORK(K)=- (EK+T)/A(K,K)
50  CONTINUE
      DO 60 KB=1,NM1
        K=N-KB
        T=0.0
        KP1=K+1
        DO 55 I=KP1,N
          T=T+A(I,K)*WORK(K)
55  CONTINUE
          WORK(K)=T
          M=IPVT(K)
          IF(M.EQ.K)GOTO 60
          T=WORK(M)
          WORK(M)=WORK(K)
          WORK(K)=T
60  CONTINUE

      YNORM=0.0
      DO 65 I=1,N
        YNORM=YNORM+ABS(WORK(I))
65  CONTINUE

SOLVE A*Z=Y

      CALL SOLVE(NDIM,N,A,WORK,IPVT)

      ZNORM=0.0
      DO 70 I=1,N
        ZNORM=ZNORM+ABS(WORK(I))
70  CONTINUE

ESTIMATE CONDITION

      COND=ANORM*ZNORM/YNORM
      IF(COND.LT.1.0)COND=1.0
      RETURN

```



```

80 COND=1.0
   IF(A(1,1).NE.0.0)RETURN

```

EXACT SINGULARITY

```

90 COND=1.0E+32
   RETURN
   END

```

SUBROUTINE SOLVE(NDIM,N,A,B,IPVT)

```

  INTEGER NDIM,N,IPVT(N)
  REAL A(NDIM,N),B(N)

```

SOLUTION OF LINEAR SYSTEM, $A \cdot X = B$
 DO NOT USE IF DECOMP HAS DETECTED SINGULARITY

INPUT:

NDIM =DECLARED ROW DIMENSION OF ARRAY CONTAINING A

N =ORDER OF MATRIX

A =TRIANGULARIZED MATRIX OBTAINED FROM DECOMP

B =RIGHT HAND SIDE VECTOR

IPVT =PIVOT VECTOR OBTAINED FROM DECOMP

OUTPUT:

B =SOLUTION VECTOR X.

```

  INTEGER KB,KM1,NM1,KP1,I,K,M
  REAL T

```

FORWARD ELIMINATION

```

  IF(N.EQ.1) GOTO 50
  NM1=N-1
  DO 20 K=1,NM1
    KP1=K+1

```



```

M=IPVT(K)
T=B(M)
B(M)=B(K)
B(K)=T
DO 10 I=KP1,N
    B(I)=B(I)+A(I,K)*T
10  CONTINUE
20  CONTINUE

```

BACK SUBSTITUTE

```

DO 40 KB=1,NM1
    KM1=N-KB
    K=KM1+1
    B(K)=B(K)/A(K,K)
    T=-B(K)
    DO 30 I=1,KM1
        B(I)=B(I)+A(I,K)*T
30  CONTINUE
40  CONTINUE
50  B(1)=B(1)/A(1,1)
    RETURN
END

```

```

SUBROUTINE NEZE(X,Y,N,NG1)
REAL X(20),Y(20),NG1(20)
TEST=1.0
DO 1 I=1,N
    IF(NG1(I)) 2,2,1
2  IF (X(I)) 3,3,1
3  SLAM=-0.99*Y(I)/(X(I)-Y(I))
    IF(SLAM-TEST)4,4,1
4  TEST=SLAM
1  CONTINUE
    DO 5, I=1,N
        IF (NG1(I)) 7,7,5
7  X(I)=Y(I)+TEST*(X(I)-Y(I))
        IF (X(I)-0.10E-10) 6,6,5
6  X(I)=0.0
        NG1(I)=1
5  CONTINUE
    RETURN
END

```


-----EES8-----

THIS IS A PROGRAM DESIGNED TO CALCULATE PRODUCTS DISTRIBUTION AND K_p OF CLAUS SYSTEM BASED ON EXPERIMENTAL DATA AND THE ASSUMPTION OF MODEL OF S8.

IMPLICIT NONE

REAL PH2O(10),NSG(10),PT,VN2,MS8(10),PH2S(10),K(10)

REAL MN2,DMH2S(10),MT(10),MH2SIN,MH2SOUT(10),VH2S

REAL H2SCOV(8),T(8),PSO2(10),PS8(10),OTPT(15,8)

INTEGER TN,I,J

DATA PT/1.0/,VN2/304.5/,VH2S/16.754/

DATA T/558.6,565.5,572.8,580.1,587.5,603.1,609.5,618.1/

DATA H2SCOV/0.9318,0.9238,0.9154,0.9060,0.9010,0.8803,

* 0.8747,0.8531/

OPEN(UNIT=7, FILE='B:RET1')

DO 10 TN=1,8

MN2=(1.0*VN2*3600.0)/(0.08205*294.13*10**3)

MH2SIN=(1.0*VH2S*3600.0)/(0.08205*294.13*10**3)

MH2SOUT(TN)=(1.0-H2SCOV(TN))*MH2SIN

DMH2S(TN)=MH2SIN-MH2SOUT(TN)

NSG=1.5*DMH2S(TN)

MS8(TN)=NSG(TN)/8

MT(TN)=MN2+MS8(TN)+1.5*MH2SOUT(TN)+DMH2S(TN)

PH2S(TN)=(MH2SOUT(TN)/MT(TN))*PT

PH2O(TN)=(DMH2S(TN)/MT(TN))*PT

PSO2(TN)=(0.5*MH2SOUT(TN)/MT(TN))*PT

PS8(TN)=(MS8(TN)/MT(TN))*PT

WRITE(6,*) PH2S(TN),PSO2(TN), PH2O(TN),PS8(TN)

K(TN)=((PS8(TN)**0.375)*(PH2O(TN)**2.0))

* /((PH2S(TN)**2.0)*PSO2(TN))

OTPT(1,TN)=T(TN)

OTPT(2,TN)=PT

OTPT(3,TN)=MH2SOUT(TN)/MT(TN)

OTPT(4,TN)=0.5*MH2SOUT(TN)/MT(TN)

OTPT(5,TN)=DMH2S(TN)/MT(TN)

OTPT(6,TN)=MS8(TN)/MT(TN)

OTPT(7,TN)=MN2/MT(TN)

OTPT(8,TN)=K(TN)

OTPT(9,TN)=1/T(TN)

OTPT(10,TN)=ALOG(K(TN))

10 CONTINUE

START TO PRINT OUT RESULTS

```
WRITE(6,300)PT
WRITE(7,300)PT
300 FORMAT('PRESSURE(KPA)=',F7.3)
WRITE(6,81)
WRITE(7,81)
81 FORMAT(2X,'TEMP(K)', 'H2S SO2 H2O S8 N2 K')
DO 666 J=1,8
WRITE(6,82)OTPT(1,J),(OTPT(I,J),I=3,8)
666 WRITE(7,82)OTPT(1,J),(OTPT(I,J),I=3,8)
82 FORMAT(2X,F6.1,5(F10.6,2X),F10.4,2X)
WRITE(6,83)
WRITE(7,83)
83 FORMAT(2X,'TEMP(K)', '1/T LOGK ')
DO 667 J=1,8
WRITE(6,84)OTPT(1,J),(OTPT(I,J),I=9,10)
667 WRITE(7,84)OTPT(1,J),(OTPT(I,J),I=9,10)
84 FORMAT(2X,F6.1,2(F10.6,2X))
STOP
END
```


-----ASAN-----

THIS IS A PROGRAM DESIGNED TO CALCULATE AVERAGE SULPHUR
ATOMIC NUMBER

IMPLICIT NONE

REAL YST(8),YS2(8),YS6(8),YS7(8),YS8(8),MT(8),MTS(8)

REAL X(8),T(8),CV(8)

INTEGER I,J

DATA YS2/0.0084,0.0109,0.0140,0.0178,0.0233,0.0378,0.0468,
* 0.0595/

DATA YS6/0.2651,0.2759,0.2865,0.2963,0.3072,0.3255,0.3332,
* 0.3409/

DATA YS7/0.1640,0.1696,0.1743,0.1799,0.1852,0.1935,0.1967,
* 0.1997/

DATA YS8/0.5312,0.5111,0.4914,0.4711,0.4486,0.4070,0.3880,
* 0.3665/

DATA CV/0.9214,0.9148,0.9077,0.9004,0.8917,0.8743,0.8658,
* 0.8557/

DATA T/558.6,565.5,572.8,580.1,587.5,603.1,609.5,618.1/

OPEN(UNIT=7, FILE='B:RETAVG')

DO 10 I=1,8

YST(I)=YS2(I)+YS6(I)+YS7(I)+YS8(I)

MT(I)=(5*(1-CV(I))+2.5*(1-CV(I))+5*CV(I)+92.5)/(1-YST(I)/100)

MTS(I)=MT(I)*YST(I)/100

X(I)=7.5*CV(I)/MTS(I)

10 CONTINUE

WRITE(6,80)

WRITE(7,80)

80 FORMAT(2X,'T(K)', 'X','MT','MTS')

DO 20 J=1,8

WRITE(6,81) T(J), X(J),MT(J),MTS(J)

20 WRITE(7,81) T(J), X(J),MT(J),MTS(J)

81 FORMAT(2X, F5.1,3(F10.4,1X))

STOP

END

APPENDIX B**CALIBRATION OF PROCESS VARIABLE MEASUREMENT DEVICES**

B-1. Mass Flow Controllers

The H₂S and SO₂ mass flow controllers were calibrated using a soap film flow meter at room temperature (about 20°C) and pressure (94.813 kPa), while the N₂ was calibrated by means of a pre-calibrated wet test meter under the same conditions. The calibration data obtained were fitted to a calibration equation of the following form,

$$Y = a_0 + a_1 X \quad (B-1)$$

where

Y = volumetric flow rate (cm³(stp)/min)

X = actual or percent reading on the mass flow controller

a₀, a₁ = calibration parameters

by applying the linear least-square curve fitting technique. The calibration results are listed in Table B-1, B-2, B-3.

B-2. Pressure Controller

The pressure controller was calibrated at room temperature and pressure with pure N₂ using a pre-calibrated Heise solid front gauge. The calibration data in the range used in this work were fitting to a straight line by means of the linear least-square curve fitting technique and the results are presented in Table B-4.

B-3 GC Calibrations

Since N₂ acted as an inert in our study, the N₂ mole flow rates in both feed and product

were the same. N_2 was used as the reference gas in calibrating GC based on the relationship between GC area and mole. The calibration curves are shown in Figure B-1 and B-2 followed by error analysis exhibited in Table B-5 and B-6.

TABLE B-1

Calibration of N₂ Mass Flow Controller

X = reading on controller

Y = flow rate (cm³/min)

The coefficients of the linear equation(B-1) are

$$a_0 = 162.051$$

$$a_1 = 0.989$$

Regenerated Data

X measured	Y observed	Y calculated	Pct Error
150	310.699	310.400	0.0965
200	361.736	359.857	0.519
250	411.143	409.315	0.445
300	456.350	458.772	0.531
400	555.790	557.687	0.341
500	655.742	656.602	0.131
600	754.452	755.518	0.141
700	854.897	854.433	0.0543
750	905.664	903.890	0.196
Standard Error of Y Calculated		1.759222	
Standard Error of Coefficient		0.002815	
R Squared		0.999886	

TABLE B-2

Calibration of H₂S Mass Flow Controller

X = reading on controller

Y = flow rate (cm³/min)

The coefficients of the linear equation(B-1) are

$$a_0 = 1.675$$

$$a_1 = 1.622$$

Regenerated Data

X measured	Y observed	Y calculated	Pct Error
10.0	17.871	17.889	0.103
15.0	25.983	25.998	0.0561
20.0	34.239	34.106	0.389
25.0	42.052	42.214	0.385
30.0	50.403	50.322	0.161
35.0	58.411	58.430	0.0329

Standard Error of Y Calculated 0.113402

Standard Error of Coefficient 0.005422

R Squared 0.999910

TABLE B-3

Calibration of SO₂ Mass Flow Controller

X = reading on controller

Y = flow rate (cm³/min)

The coefficients of the linear equation(B-1) are

$$a_0 = 0.617$$

$$a_1 = 1.113$$

Regenerated Data

X measured	Y observed	Y calculated	Pct Error
5.0	6.31	6.18	2.06
10.0	11.76	11.75	0.0568
15.0	15.88	16.21	2.10
20.0	23.08	22.90	0.800

Standard Error of Y Calculated	0.253357
Standard Error of Coefficient	0.025686
R Squared	0.997875

TABLE B-4

Calibration of Pressure Controller

X = reading on controller

Y = Pressure (psig)

The coefficients of the linear equation(B-1) are

$$a_0 = -0.851$$

$$a_1 = 1.027$$

Regenerated Data

X measured	Y observed	Y calculated	Pct Error
1.0	0.175	0.18	2.86
2.0	1.225	1.203	1.80
3.5	2.75	2.745	0.20
5.0	4.25	4.286	0.84
7.0	6.375	6.340	0.54

Standard Error of Y Calculated	0.068599
Standard Error of Coefficient	0.014366
R Squared	0.998828

Figure B-1

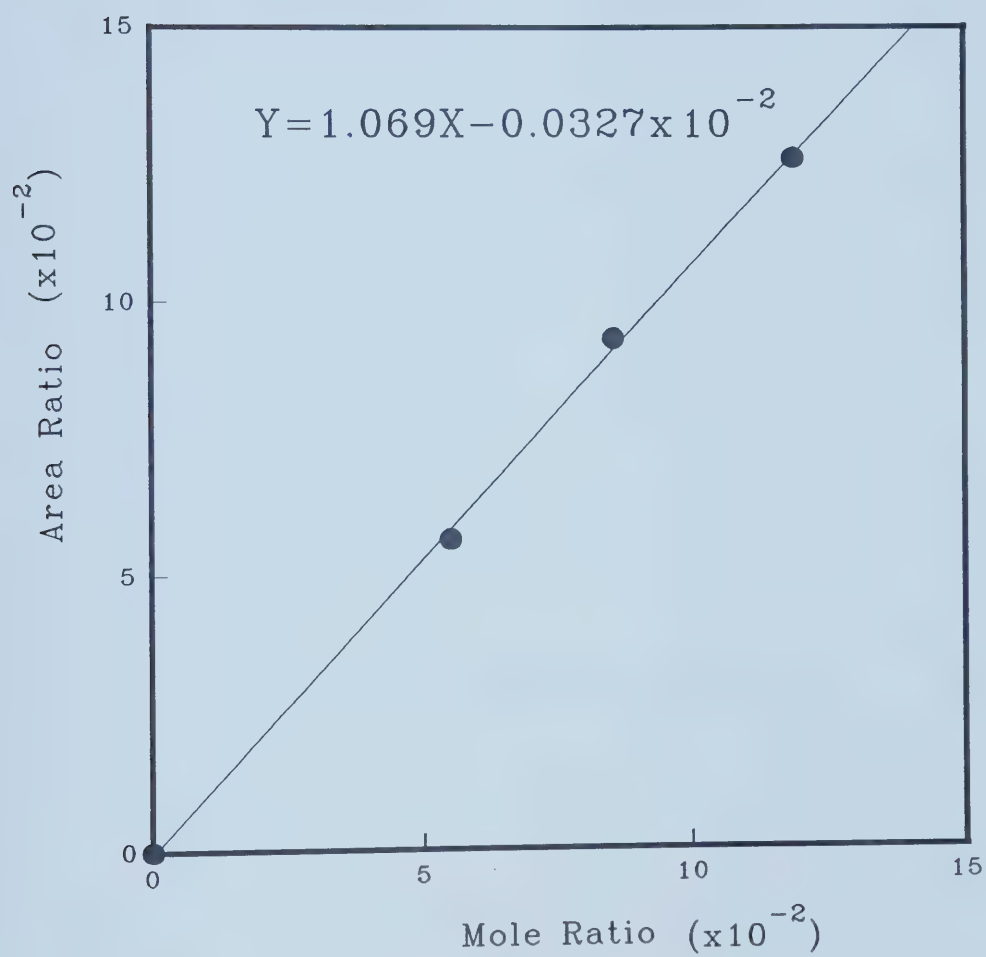
GC Calibration For $\text{H}_2\text{S}/\text{N}_2$ System

Figure B-2

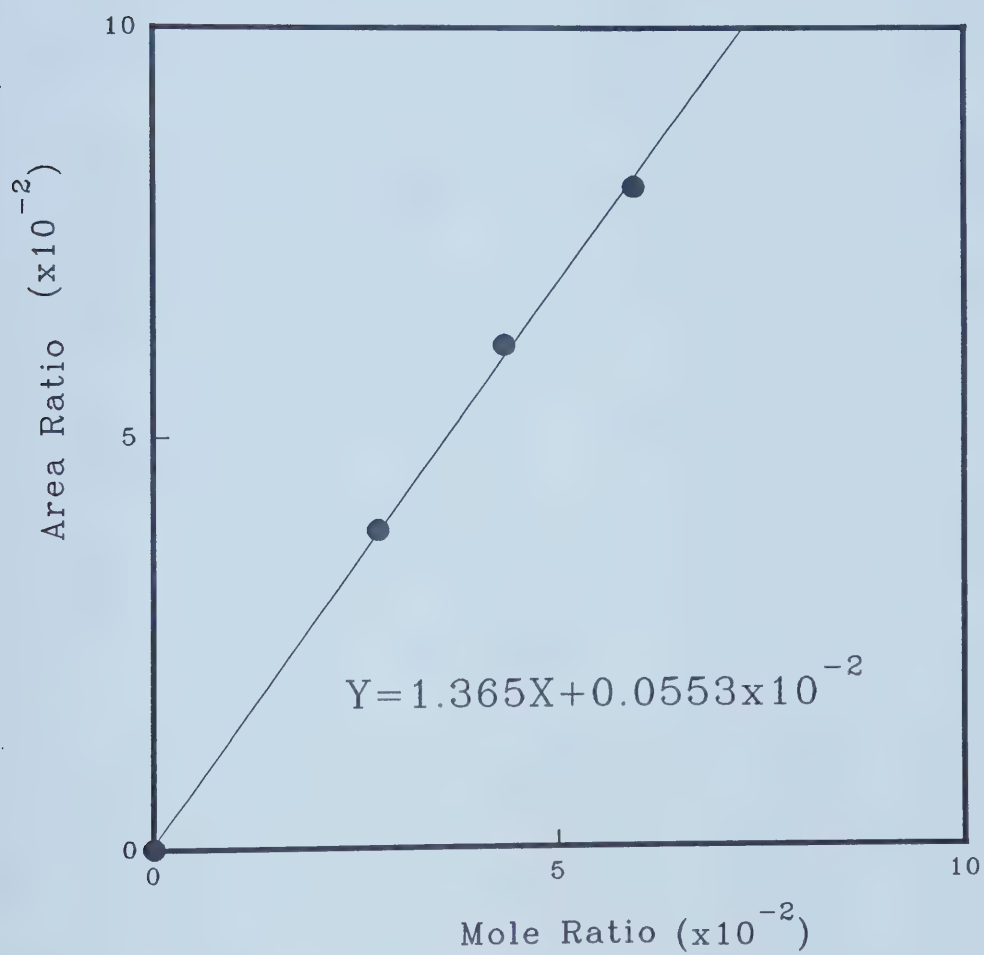
GC Calibration For SO_2/N_2 System

TABLE B-6

GC Calibration of SO₂/N₂ System

X = Mole ratio

Y = Area ratio

The coefficients of the linear equation(B-1) are

$$a_0 = 0.0553 \times 10^{-2}$$

$$a_1 = 1.365$$

Regenerated Data

X measured	Y observed	Y calculated	Pct Error
0.000	0.000	0.000553	---
0.0276	0.0386	0.0377	2.332
0.0434	0.0611	0.0592	3.110
0.0594	0.0805	0.0811	0.745
Standard Error of Y Calculated		0.001595	
R Squared		0.99898	

APPENDIX C

SAMPLE CALCULATIONS

SAMPLE CALCULATION FOR EXPERIMENTAL K_p BASED ON SINGLE SULPHUR MOLECULAR MODEL OF S_8

Experimental Information:

Feed Composition: H_2S : 5.0%, SO_2 : 2.5%, N_2 : 92.5%

Reaction Temperature: 603.1 K (oven temperature)

Reaction Pressure: 101.33 kPa (measured at tube outlet)

H_2S Conversion(γ): 88.03%

If we assume 5 moles of H_2S react with 2.5 moles of SO_2 in reaction (3-16),



the product distribution for each species at equilibrium would be:

$$M_{H_2S} = 5.0(1-\gamma) = 0.596 \text{ (mol)}$$

$$M_{SO_2} = 2.5(1-\gamma) = 0.299 \text{ (mol)}$$

$$M_{H_2O} = 5.0\gamma = 4.402 \text{ (mol)}$$

$$M_{S_8} = 7.5\gamma/8 = 0.825 \text{ (mol)}$$

the total moles in the product mixture is then:

$$M_T = \sum M_j \quad (j=N_2, H_2S, SO_2, H_2O \text{ and } S_8)$$

$$\begin{aligned} M_T &= 92.5 + 0.596 + 0.299 + 4.402 + 0.825 \\ &= 98.625 \text{ (mol)} \end{aligned}$$

and in turn: from equation

$$Y_j = M_j/M_T$$

$$Y_{H_2S} = 6.066 \times 10^{-3}$$

$$Y_{SO_2} = 3.034 \times 10^{-3}$$

$$Y_{H_2O} = 4.463 \times 10^{-2}$$

$$Y_{S_8} = 8.368 \times 10^{-3}$$

finally, the equilibrium constant

$$K_{P_1} = \frac{\left[\frac{M_{H_2O}}{M_T} \right]^2 \left[\frac{M_{S_8}}{M_T} \right]^{\frac{3}{8}}}{\left[\frac{M_{H_2S}}{M_T} \right]^2 \left[\frac{M_{SO_2}}{M_T} \right]} P^{-\frac{5}{8}} \quad (3-20)$$

$$= 2934$$

SAMPLE CALCULATION FOR AVERAGE SULPHUR ATOMIC NUMBER BASED ON THERMODYNAMIC PREDICTION

Information from Thermodynamic Prediction:

Feed Composition: H_2S : 5.0%, SO_2 : 2.5%, N_2 : 92.5%

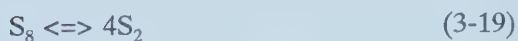
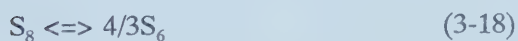
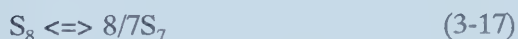
Reaction Temperature: 603.1 K

Reaction Pressure: 101.33 kPa

Product Distribution(mol%): Y_i (please see below)

H_2S Conversion(γ): 87.43%

If we assume 5 moles of H_2S react with 2.5 moles of SO_2 in reactions (3-16)-(3-19),



the thermodynamic predicted product distribution (mol%) would be:

$$Y_{\text{H}_2\text{S}} = 0.637$$

$$Y_{\text{SO}_2} = 0.318$$

$$Y_{\text{H}_2\text{O}} = 4.426$$

$$Y_{\text{S}_2} = 0.0378$$

$$Y_{\text{S}_6} = 0.326$$

$$Y_{\text{S}_7} = 0.194$$

$$Y_{S8} = 0.407$$

$$Y_{N2} = 93.656$$

Since total moles in the product are

$$M_T = M_{H2S} + M_{SO2} + M_{H2O} + M_{N2} + \sum M_{S_n}$$

$$(n=2, 6, 7 \text{ and } 8)$$

$$= 5(1-\gamma) + 2.5(1-\gamma) + 5\gamma + 92.5 + M_T \sum Y_{S_n}$$

so, $M_T = 98.767 \text{ (mol)}$

in turn, total moles of sulphur vapour,

$$M_{Ts} = M_T \sum Y_{S_n}$$

$$= 0.953 \text{ (mol)}$$

and from total sulphur gram-atom number, which is

$$N_{Sg} = 7.5\gamma$$

we finally can calculate average atomic number X,

$$X = N_{Sg} / M_{Ts} = 6.889$$

APPENDIX D

EXPERIMENTAL DATA

RAW DATA

RUN #	TEMP. (K)	PRESSURE(Psia)		FEED FLOW (cm ³ /min)			GC RESULT	
		INLET	OUTLET	N ₂	H ₂ S	SO ₂	(A _{H2S} /A _{N2}) _F	(A _{H2S} /A _{N2}) _P
1	558.6	39.245	15.745	305	16.8	8.4	5.663x10 ⁻²	3.865x10 ⁻³
2	565.5	37.870	16.995	305	16.8	8.4	5.966x10 ⁻²	4.547x10 ⁻³
3	572.8	39.495	14.745	305	16.8	8.4	5.633x10 ⁻²	4.765x10 ⁻³
4	580.1	38.495	16.245	305	16.8	8.4	5.661x10 ⁻²	5.322x10 ⁻³
5	587.5	39.395	15.445	305	16.8	8.4	5.647x10 ⁻²	5.590x10 ⁻³
6	603.1	40.995	13.745	305	16.8	8.4	5.748x10 ⁻²	6.835x10 ⁻³
7	609.5	38.120	16.995	305	16.8	8.4	5.498x10 ⁻²	6.887x10 ⁻³
8	618.1	41.995	13.745	305	16.8	8.4	5.560x10 ⁻²	8.166x10 ⁻³
9	559.1	38.850	15.885	292	25.2	12.6	9.365x10 ⁻²	6.265x10 ⁻³
10	566.3	38.245	16.445	292	25.2	12.6	9.310x10 ⁻²	7.411x10 ⁻³
11	579.7	38.745	16.095	292	25.2	12.6	9.350x10 ⁻²	8.959x10 ⁻³
12	610.4	38.120	16.995	292	25.2	12.6	9.423x10 ⁻²	1.154x10 ⁻²
13	559.3	39.495	15.995	280	33.3	16.6	1.216x10 ⁻¹	8.200x10 ⁻³
14	566.4	37.745	17.145	280	33.3	16.6	1.328x10 ⁻¹	9.681x10 ⁻³
15	580.0	37.995	16.845	280	33.3	16.6	1.234x10 ⁻¹	1.139x10 ⁻²

RAW DATA (CONTINUE)

RUN #	TEMP. (K)	PRESSURE(Psia)		FEED FLOW (cm ³ /min)			GC RESULT	
		INLET	OUTLET	N ₂	H ₂ S	SO ₂	(A _{H2S} /A _{N2}) _F	(A _{H2S} /A _{N2}) _P
16	588.4	40.245	14.745	280	33.3	16.6	1.261x10 ⁻¹	1.329x10 ⁻²
17	603.5	39.995	15.495	280	33.3	16.6	1.228x10 ⁻¹	1.499x10 ⁻²
18	618.2	39.745	14.870	280	33.3	16.6	1.271x10 ⁻¹	1.858x10 ⁻²
19	632.3	40.245	14.495	280	33.3	16.6	1.273x10 ⁻¹	2.049x10 ⁻²
20	559.2	34.850	20.146	196	16.8	8.4	9.216x10 ⁻²	6.258x10 ⁻³
21	610.1	34.120	20.745	160	16.8	8.4	9.188x10 ⁻²	1.114x10 ⁻²
22	558.8	35.025	20.145	391	33.6	16.8	9.376x10 ⁻²	6.441x10 ⁻³
23	610.3	35.385	19.670	391	33.6	16.8	9.398x10 ⁻²	1.148x10 ⁻²
24	558.6	40.745	13.745	297	25.2	8.4	9.040x10 ⁻²	3.264x10 ⁻²
25	573.2	40.745	14.745	297	25.2	8.4	9.140x10 ⁻²	3.344x10 ⁻²
26	603.1	41.245	13.745	297	25.2	8.4	9.032x10 ⁻²	3.369x10 ⁻²
27	617.8	40.495	14.495	297	25.2	8.4	9.048x10 ⁻²	3.369x10 ⁻²

PROCESSED DATA

RUN	TEMP.	PRESSURE	FEED COMPOSITION			S.V.	CONVERSION
#	(K)	(kPa)	N ₂	H ₂ S	SO ₂	(h ⁻¹)	(H ₂ S)
1	558.6	108.562	92.5	5.0	2.5	364	93.18
2	565.5	117.212	92.5	5.0	2.5	364	92.38
3	572.8	101.667	92.5	5.0	2.5	364	91.54
4	580.1	112.009	92.5	5.0	2.5	364	90.60
5	587.5	106.493	92.5	5.0	2.5	364	90.10
6	603.1	94.772	92.5	5.0	2.5	364	88.03
7	609.5	117.181	92.5	5.0	2.5	364	87.47
8	618.1	94.772	92.5	5.0	2.5	364	85.31
9	559.1	109.527	88.6	7.6	3.8	364	93.31
10	566.3	113.388	88.6	7.6	3.8	364	92.04
11	579.7	110.975	88.6	7.6	3.8	364	90.42
12	610.4	117.181	88.6	7.6	3.8	364	87.75
13	559.3	110.286	88.0	10.0	5.0	364	93.26
14	566.4	118.215	88.0	10.0	5.0	364	92.71
15	580.0	116.146	88.0	10.0	5.0	364	90.77

PROCESSED DATA (CONTINUE)

RUN	TEMP.	PRESSURE	FEED COMPOSITION			S.V.	CONVERSION
#	(K)	(kPa)	N ₂	H ₂ S	SO ₂	(h ⁻¹)	(H ₂ S)
16	588.4	101.667	88.0	10.0	5.0	364	89.46
17	603.5	106.838	88.0	10.0	5.0	364	87.79
18	618.2	102.529	88.0	10.0	5.0	364	85.38
19	632.3	99.943	88.0	10.0	5.0	364	83.90
20	559.2	138.907	88.6	7.6	3.8	242	93.21
21	610.1	143.037	88.6	7.6	3.8	242	87.87
22	558.8	138.900	88.6	7.6	3.8	486	93.13
23	610.3	135.623	88.6	7.6	3.8	486	87.78
24	558.6	94.772	89.9	7.6	2.5	364	63.89
25	573.2	101.667	89.9	7.6	2.5	364	63.42
26	603.1	94.772	89.9	7.6	2.5	364	62.70
27	617.8	99.943	89.9	7.6	2.5	364	62.77

APPENDIX E

MATHEMATICAL DEDUCTION OF EFFECT OF FEED COMPOSITION UPON EQUILIBRIUM CONVERSION

Assumptions and Conditions:

Ideal gas mixture behaviour

 P_T is constant K_p is only dependent on temperature

Total moles in feed mixture: 100

Total moles of H_2S in feed: ATotal moles of SO_2 in feed: A/2Fractional H_2S conversion: γ

For the exothermic part of the modified Claus reaction in Figure 5-6 ($T < 800$ K), assume that reaction



applies.

Then, $M_T = 100 - 3/2A + A(1-\gamma) + A/2(1-\gamma) + 3/16A\gamma + A\gamma = 100 - 5/16A\gamma$

$$K_P = K_P P_T^{-\frac{5}{8}} = \frac{\left(\frac{3}{16}A\gamma\right)^{\frac{3}{8}} \left[\frac{(A\gamma)^2}{M_T}\right]^{\frac{1}{2}} P_T^{-\frac{5}{8}}}{\left[\frac{A(1-\gamma)^2}{M_T}\right] \left[\frac{\frac{A}{2}(1-\gamma)}{M_T}\right]}$$

$$= 2\left(\frac{3}{16}\right)^{\frac{3}{8}} \frac{\gamma^{\frac{2\frac{3}{8}}{8}}}{(1-\gamma)^3} \left(\frac{100}{A} - \frac{5}{16}\gamma\right)^{\frac{5}{8}} P_T^{-\frac{5}{8}} = BCD$$

$$\text{where, } B=2\left(\frac{3}{16}\right)^{\frac{3}{8}}P_T^{-\frac{5}{8}}=\text{constant} \quad C=\frac{\gamma^{\frac{2\frac{3}{8}}{8}}}{(1-\gamma)^3} \quad D=\left(\frac{100}{A}-\frac{5}{16}\gamma\right)^{\frac{5}{8}}$$

Since

$$\frac{dC}{d\gamma} = \frac{\left[2\frac{3}{8}(1-\gamma)^3\gamma^{1\frac{3}{8}}\right] + \left[3\gamma^{\frac{2\frac{3}{8}}{8}}(1-\gamma)^2\right]}{(1-\gamma)^6} > 0,$$

C is increasing with increasing conversion, γ . And also since increasing A results in the decreasing of D, γ must then be increased, which makes C increased, to keep K_p constant. In other words, a higher feed composition would lead to a higher conversion under constant reaction temperature and pressure.

By the same token, if reaction



applies for the endothermic part of the modified Claus reaction in Figure 5-6 ($T > 800\text{K}$),

Then

$$M_T = 100 - 3/2A + A(1-\gamma) + A/2(1-\gamma) + 3/4A\gamma + A\gamma = 100 + 1/4A\gamma$$

$$K_P = K_T P_T^{\frac{1}{2}} = \frac{\left[\frac{\left(\frac{3}{4}A\gamma\right)^{\frac{3}{2}}}{M_T}\right] \left[\frac{(A\gamma)^2}{M_T}\right] P_T^{\frac{1}{2}}}{\left[\frac{A(1-\gamma)^2}{M_T}\right] \left[\frac{\frac{A}{2}(1-\gamma)}{M_T}\right]}$$

$$= 2\left(\frac{3}{4}\right)^{\frac{3}{2}} \frac{\gamma^{\frac{3}{2}}}{(1-\gamma)^3} \frac{1}{\left(\frac{100}{A} + \frac{\gamma}{4}\right)^{\frac{1}{2}}} P_T^{\frac{1}{2}} = EFG$$

$$\text{where,} \quad E = 2\left(\frac{3}{4}\right)^{\frac{3}{2}} P_T^{\frac{1}{2}} = \text{constant} \quad F = \frac{\gamma^{\frac{3}{2}}}{(1-\gamma)^3} \quad G = \frac{1}{\left(\frac{100}{A} + \frac{\gamma}{4}\right)^{\frac{1}{2}}}$$

Since

$$\frac{dF}{d\gamma} = \frac{\left[3\frac{1}{2}(1-\gamma)^3\gamma^{\frac{1}{2}}\right] + \left[3\gamma^{\frac{3}{2}}(1-\gamma)^2\right]}{(1-\gamma)^6} > 0,$$

F is increasing with increasing conversion, γ . And also since increasing A results in the increasing of G, γ must then be decreased, which makes F decreased, to keep K_p constant. In other words, a higher feed composition would lead to a lower conversion under constant reaction temperature and pressure.

APPENDIX F

ERROR ANALYSIS

The following factors may cause an error in the calculation of experimental conversions in this work: (1) errors in flow rates for both H_2S and N_2 caused by calibrations of mass flow controllers and accuracy of the controllers themselves; (2) an error existed in calibration of G.C. representing the relationship between mole ratio and area ratio; and (3) an error corresponding to G.C. analysis.

We will use the experimental conversion under feed composition of H_2S : 5.0%, SO_2 : 2.5% and N_2 : 92.5% at 580.1 K as an example to estimate the overall error in experimental conversion data. In this particular case, the flow rates for H_2S and N_2 were 16.8 and 305 (cm^3/min), respectively.

From standard errors of mass flow controllers' calibration equations listed in Appendix B and accuracy of both controllers, an accumulated error in flow rate could be calculated as following:

	H_2S (cm^3/min)	N_2 (cm^3/min)
Flow rate	16.8	305
Error in Calibration	± 0.113	± 1.759
Error in accuracy	± 0.1	± 1
Accumulated Error	± 0.213	± 2.759
Accumulated Error (conservative value)	± 0.3	± 3

The mole ratios between H_2S and N_2 of the feed mixture then were:

$$M_{H2S}/M_{N2} = 16.8/305 = 5.508 \times 10^{-2}$$

$$(M_{H2S}/M_{N2})_{min.} = (16.8-0.3)/(305+3) = 5.357 \times 10^{-2}$$

$$(M_{H2S}/M_{N2})_{max.} = (16.8+0.3)/(305-3) = 5.662 \times 10^{-2}$$

From G.C. calibration equation between mole ratio (M_{H2S}/M_{N2}) and area ratio (A_{H2S}/A_{N2}), and the associated standard error, the corresponding area ratios for $(M_{H2S}/M_{N2})_{min.}$ and $(M_{H2S}/M_{N2})_{max.}$ of the feed mixture could be calculated as follows:

	$(M_{H2S}/M_{N2})_{min.}$	$(M_{H2S}/M_{N2})_{max.}$
Area Ratio from Calibration	5.694×10^{-2}	6.052×10^{-2}
Error from Calibration	$\pm 2.545 \times 10^{-3}$	$\pm 2.545 \times 10^{-3}$
Area Ratio with Error	5.440×10^{-2}	6.307×10^{-2}

From G.C. analysis, the area ratios (A_{H2S}/A_{N2}) of both feed and product mixtures with analysis error limits could be obtained. The detailed procedure is presented as follows:

NOMENCLATURE: I	An observation
$\bar{I}$	The average of a number of observations
f	Degree of freedom
s	The standard deviation of a sample
CL	Confidence limits
t	The critical value of the t test (Bauer, 1960)
n	Number of samples

$(A_{\text{H}_2\text{S}}/A_{\text{N}_2})_{\text{Feed}}(\text{I})$	$(\text{I}-\bar{\text{I}})$	$(\text{I}-\bar{\text{I}})^2$
5.66060×10^{-2}	3.300×10^{-6}	1.100×10^{-11}
5.66122×10^{-2}	2.900×10^{-6}	0.800×10^{-11}
5.66095×10^{-2}	0.200×10^{-6}	0.004×10^{-11}

$$\bar{\text{I}} = 5.66093 \times 10^{-2}$$

$$\Sigma = 1.904 \times 10^{-11}$$

$$s^2 = \Sigma(\text{I}-\bar{\text{I}})^2 / f = 1.904 \times 10^{-11} / 2$$

$$s = 3.085 \times 10^{-6}$$

$$\begin{aligned} 95\text{CL} = \bar{\text{I}} \pm st/(n)^{1/2} &= 5.66093 \times 10^{-2} \pm 3.085 \times 10^{-6} \times 4.303 / (3)^{1/2} \\ &= 5.660 \times 10^{-2} \text{---} 5.662 \times 10^{-2} \end{aligned}$$

$(A_{\text{H}_2\text{S}}/A_{\text{N}_2})_{\text{Product}}(\text{I})$	$(\text{I}-\bar{\text{I}})$	$(\text{I}-\bar{\text{I}})^2$
5.32623×10^{-3}	8.531×10^{-5}	7.27779×10^{-9}
5.33628×10^{-3}	1.474×10^{-5}	0.21727×10^{-9}
5.30210×10^{-3}	1.944×10^{-5}	0.37791×10^{-9}

$$\bar{\text{I}} = 5.32154 \times 10^{-3}$$

$$\Sigma = 7.87298 \times 10^{-9}$$

$$s = 6.27415 \times 10^{-5}$$

$$\begin{aligned} 95\text{CL} &= 5.32154 \times 10^{-3} \pm 1.55876 \times 10^{-4} \\ &= 5.166 \times 10^{-3} \text{---} 5.477 \times 10^{-3} \end{aligned}$$

From the above calculation, it is evident that the analysis error limits for $A_{\text{H}_2\text{S}}/A_{\text{N}_2}$ of feed

mixture are well covered by the previously discussed error limits which were estimated from the calibrations of G.C. and mass flow controllers and which would be used for calculating the error limits for conversion. The results are tabulated as follows:

	$(A_{\text{H}_2\text{S}}/A_{\text{N}_2})$	$(A_{\text{H}_2\text{S}}/A_{\text{N}_2})_{\text{min.}}$	$(A_{\text{H}_2\text{S}}/A_{\text{N}_2})_{\text{max.}}$
Feed	5.661×10^{-2}	5.440×10^{-2}	6.307×10^{-2}
Product	5.323×10^{-3}	5.166×10^{-3}	5.477×10^{-3}
Conversion		90.60%	
Conversion _{min.}		89.93%	
Conversion _{max.}		91.77%	

CONVERSION DATA WITH ERROR LIMITS

Feed Composition: $\text{H}_2\text{S}=5.0\%$ $\text{SO}_2=2.5\%$ $\text{N}_2=92.5\%$

Temperature (K)	Conversion (%)
	+0.63
558.6	93.18
	-0.40
	+0.45
565.5	92.38
	-0.83
	+1.05
572.8	91.54
	-0.41
	+1.11
581.1	90.60
	-0.67
	+1.13
587.5	90.10
	-0.54
	+1.27
603.1	88.03
	-0.77
	+1.71
609.5	87.47
	-0.31
	+1.89
618.1	85.31
	-0.57

Feed Composition: $\text{H}_2\text{S}=7.6\%$ $\text{SO}_2=3.8\%$ $\text{N}_2=88.6\%$

Temperature (K) Conversion (%)

	+0.61
559.1	93.31
	-0.31

	+0.66
566.3	92.04
	-0.44

	+1.02
579.7	90.42
	-0.55

	+1.25
610.4	87.75
	-0.45

Feed Composition: $\text{H}_2\text{S}=5.0\%$ $\text{SO}_2=2.5\%$ $\text{N}_2=92.5\%$

Temperature (K) Conversion (%)

	+0.59
559.3	93.26
	-0.06

	+0.04
566.4	92.71
	-0.75

	+0.87
580.0	90.77
	-1.03

	+0.58
588.4	89.46
	-1.03

	+1.16
603.5	87.79
	-0.29

	+0.82
618.2	85.38
	-0.94

	+0.67
632.3	83.90
	-0.86

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